12 Structure Determination: Mass Spectrometry and Infrared Spectroscopy

CONTENTS

12-1 Mass Spectrometry of Small Molecules: Magnetic-Sector Instruments

12-2 Interpreting Mass Spectra

12-3 Mass Spectrometry of Some Common Functional Groups

12-4 Mass Spectrometry in Biological Chemistry: Time-of-Flight (TOF) Instruments

12-5 Spectroscopy and the Electromagnetic Spectrum

12-6 Infrared Spectroscopy

12-7 Interpreting Infrared Spectra

12-8 Infrared Spectra of Some Common Functional Groups

SOMETHING EXTRA
X-Ray Crystallography

MakEni's photo/Getty Images

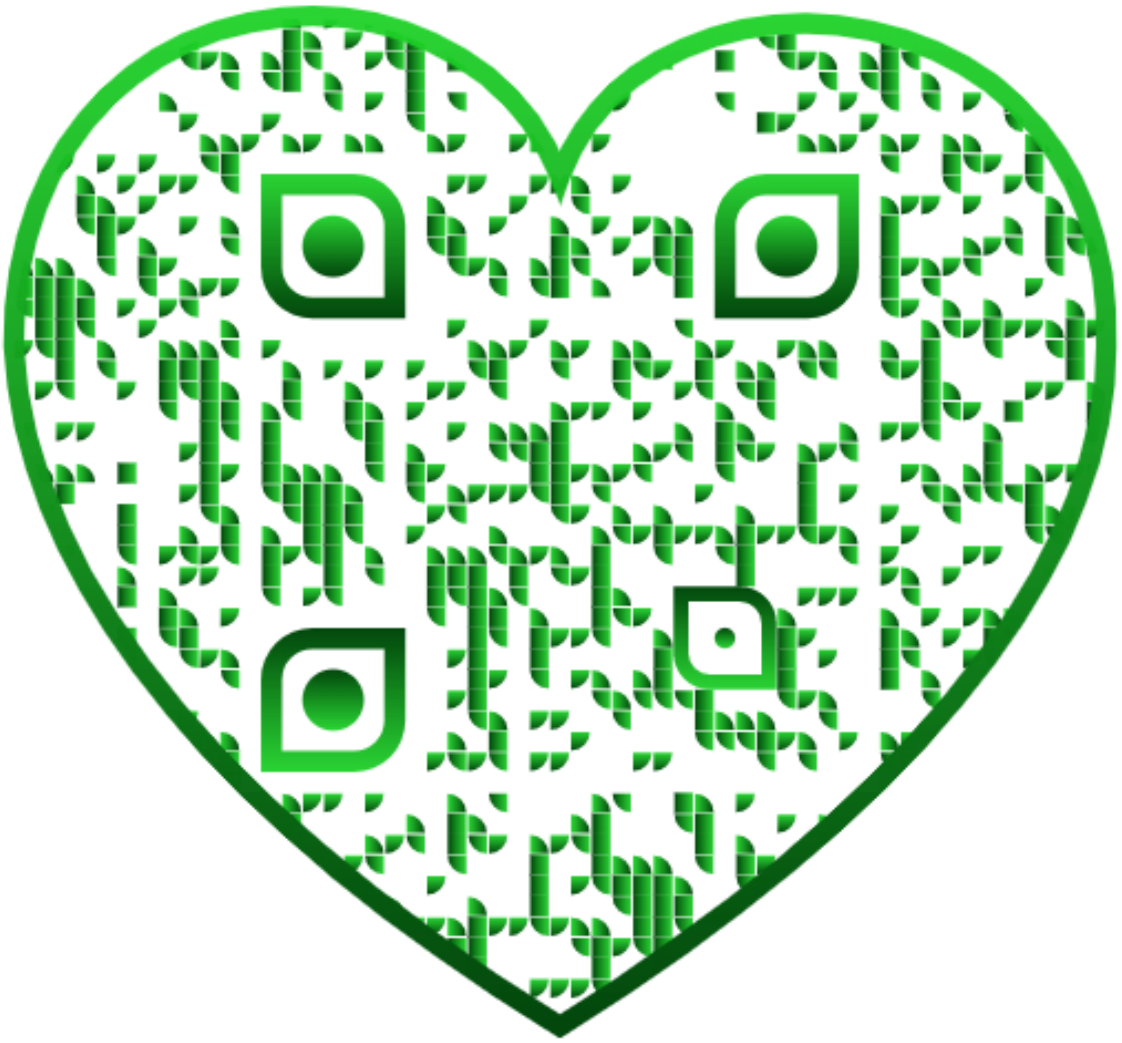
More than a thousand different chemical compounds have been isolated from coffee. Their structures were determined using various spectroscopic techniques.

WHY THIS CHAPTER? Finding the structures of new molecules, whether small ones synthesized in the laboratory or large proteins and nucleic acids found in living organisms, is central to the progression of chemistry and biochemistry. We can only scratch the surface of structure determination in this book, but after reading this and the following two chapters, you should have a good idea of the range of structural techniques available and of how and when each is used.

Every time a reaction is run, the products must be identified, and every time a new compound is found in nature, its structure must be determined. Determining the structure of an organic compound was a difficult and time-consuming process until the mid-20th century, but powerful techniques and specialized instruments are now routinely used to simplify the problem. In this and the next two chapters, we'll look at four such techniques—mass spectrometry (MS), infrared (IR) spectroscopy, ultraviolet spectroscopy (UV), and nuclear magnetic resonance spectroscopy (NMR)—and we'll see the kind of information that can be obtained from each.

Mass spectrometry	What is the size and formula?
Infrared spectroscopy	What functional groups are present?
Ultraviolet spectroscopy	Is a conjugated π electron system present?
Nuclear magnetic resonance spectroscopy	What is the carbon–hydrogen framework?

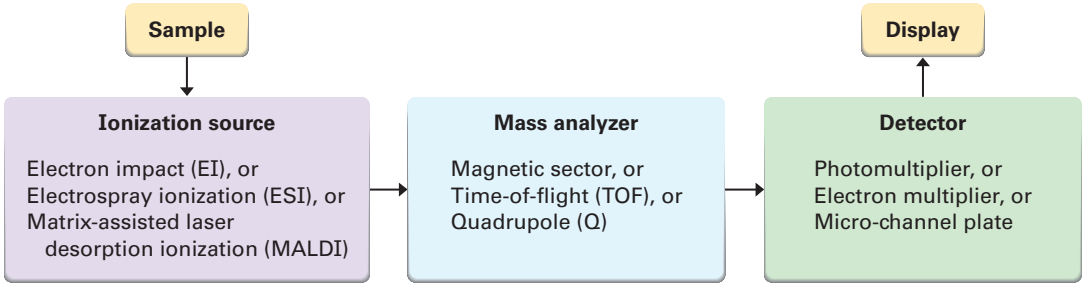
Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.



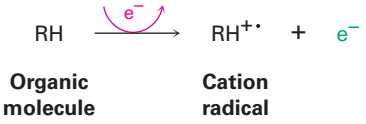
12-1 Mass Spectrometry of Small Molecules: Magnetic-Sector Instruments

At its simplest, **mass spectrometry (MS)** is a technique for measuring the mass, and therefore the molecular weight (MW), of a molecule. In addition, it's often possible to gain structural information about a molecule by measuring the masses of the fragments produced when molecules are broken apart.

More than 20 different kinds of commercial mass spectrometers are available depending on the intended application, but all have three basic parts: an *ionization source* in which sample molecules are given an electrical charge, a *mass analyzer* in which ions are separated by their mass-to-charge ratio, and a *detector* in which the separated ions are observed and counted.



Among the most common mass spectrometers used for routine purposes in the laboratory is the electron-impact, magnetic-sector instrument shown schematically in FIGURE 12-1. A small amount of sample is vaporized into the ionization source, where it is bombarded by a stream of high-energy electrons. The energy of the electron beam can be varied but is commonly around 70 electron volts (eV), or 6700 kJ/mol. When a high-energy electron strikes an organic molecule, it dislodges a valence electron from the molecule, producing a *cation radical*—*cation* because the molecule has lost an electron and now has a positive charge; *radical* because the molecule now has an odd number of electrons.



Electron bombardment transfers so much energy that most of the cation radicals fragment after formation. They break apart into smaller pieces, some of which retain the positive charge and some of which are neutral. The fragments then flow through a curved pipe in a strong magnetic field, which deflects them into different paths according to their mass-to-charge ratio (m/z). Neutral fragments are not deflected by the magnetic field and are lost on the walls of the pipe, but positively charged fragments are sorted by the mass spectrometer onto a detector, which records them as peaks at the various m/z ratios. Since the number of charges z on each ion is usually 1, the value of

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

m/z for each ion is simply its mass m. Masses up to approximately 2500 atomic mass units (amu) can be analyzed by this type of instrument.

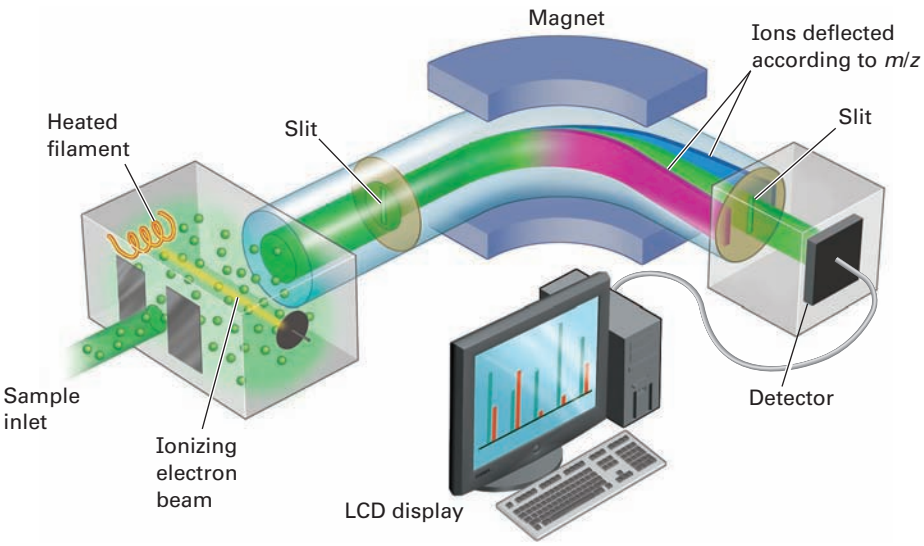


FIGURE 12-1 A representation of an electron-ionization, magnetic-sector mass spectrometer. Molecules are ionized by collision with high-energy electrons, causing some of the molecules to fragment. Passage of the charged fragments through a magnetic field then sorts them according to their mass.

Another common type of mass spectrometer uses a **quadrupole mass analyzer**. In this type of system, a set of four solid rods is arranged parallel to the direction of the ion beam. An oscillating electrostatic field is generated in the space between the rods. For a given field, only one m/z value will make it through the quadrupole region—the others will crash into the quadrupole rods or the walls of the instrument and never reach the detector. The resolution of the quadrupole system is similar to that of the magnetic-sector instrument. **FIGURE 12-2** shows a quadrupole mass analyzer.

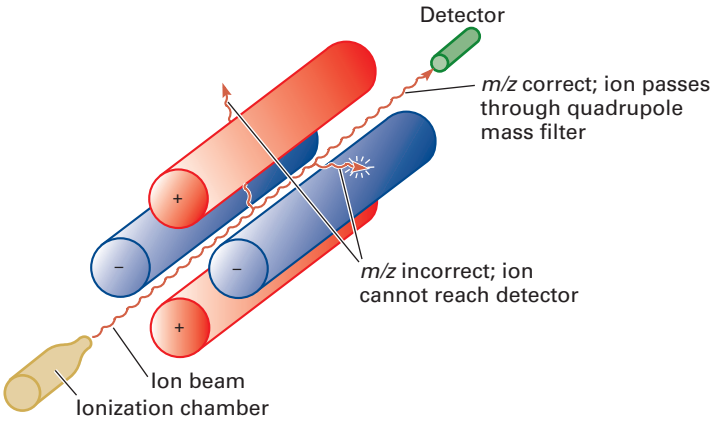


FIGURE 12-2 A representation of a quadrupole mass analyzer. Only ions of a certain m/z ratio will reach the detector; other ions with unstable trajectories will collide with the rods.

The mass spectrum of a compound is typically presented as a bar graph, with masses (m/z values) on the x axis and intensity, or relative abundance of ions of a given m/z striking the detector, on the y axis. The tallest peak, assigned an intensity of 100%, is called the **base peak**, and the peak that

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

corresponds to the unfragmented cation radical is called the **parent peak**, or the *molecular ion* (M^+, or simply M). FIGURE 12-3 shows the mass spectrum of propane.

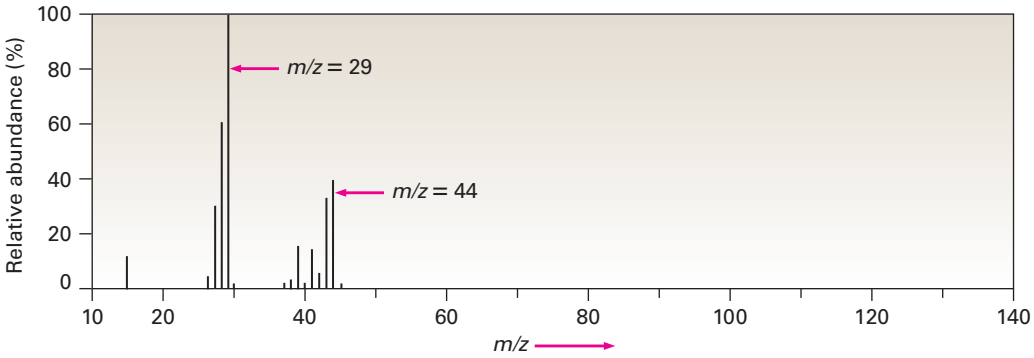


FIGURE 12-3 Mass spectrum of propane (C_3H_8; MW = 44).

Mass spectral fragmentation patterns are usually complex, and the molecular ion is often not the base peak. The mass spectrum of propane in Figure 12-3, for instance, shows a molecular ion at $m/z = 44$ that is only about 30% as high as the base peak at $m/z = 29$. In addition, many other fragment ions are present.

12-2 Interpreting Mass Spectra

What kinds of information can we get from a mass spectrum? The most obvious information is the molecular weight of the sample, which in itself can be invaluable. If we were given samples of hexane (MW = 86), 1-hexene (MW = 84), and 1-hexyne (MW = 82), for example, mass spectrometry would easily distinguish them.

Some instruments, called *double-focusing mass spectrometers,* have two magnetic sectors in their mass analyzers. These spectrometers have such high resolution that they provide mass measurements accurate to 5 ppm, or about 0.0005 amu, making it possible to distinguish between two formulas with the same nominal mass. For example, both C_5H_{12} and C_4H_8O have MW=72, but they differ slightly beyond the decimal point: C_5H_{12} has an exact mass of 72.0939 amu, whereas C_4H_8O has an exact mass of 72.0575 amu. A high-resolution instrument can easily distinguish between them. Note, however, that exact mass measurements refer to molecules with *specific isotopic compositions*. Thus, the sum of the exact atomic masses of the specific isotopes in a molecule is measured—1.007 83 amu for ^1H, 12.000 00 amu for ^{12}C, 14.003 07 amu for ^{14}N, 15.994 91 amu for ^{16}O, and so on—rather than the sum of the average atomic masses of elements, as found on a periodic table.

Unfortunately, not every compound shows a molecular ion in its electron-impact mass spectrum. Although M^+ is usually easy to identify if it's abundant, some compounds, such as 2,2-dimethylpropane, fragment so easily that

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

no molecular ion is observed (FIGURE 12-4). In such cases, alternative "soft" ionization methods that do not use electron bombardment can prevent or minimize fragmentation (see Section 12-4).

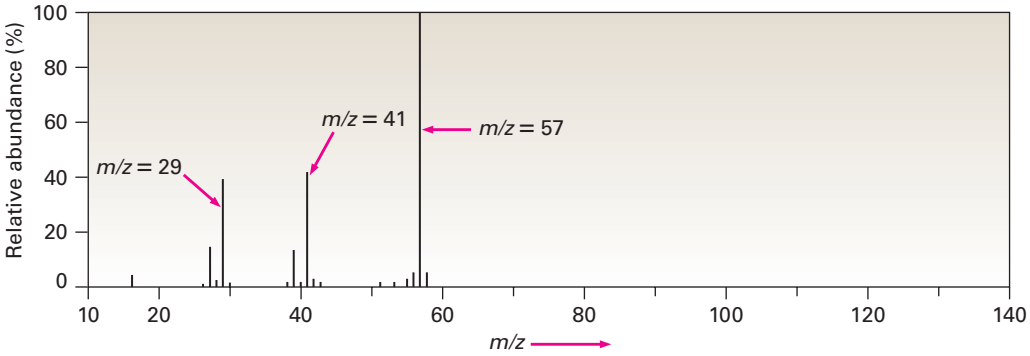


FIGURE 12-4 Mass spectrum of 2,2-dimethylpropane (C_5H_{12}; MW = 72). No molecular ion is observed when electron-impact ionization is used. What do you think is the formula and structure of the M^+ peak at $m/z = 57$?

Knowing the molecular weight makes it possible to considerably narrow the choices of molecular formula. For example, if the mass spectrum of an unknown compound shows a molecular ion at $m/z = 110$, the molecular formula is likely to be C_8H_{14}, $C_7H_{10}O$, $C_6H_6O_2$, or $C_6H_{10}N_2$. There are always a number of molecular formulas possible for all but the lowest molecular weights; a computer can easily generate a list of these choices.

A further point about mass spectrometry, noticeable in the spectra of both propane (Figure 12-3) and 2,2-dimethylpropane (Figure 12-4), is that the peak for the molecular ion is not at the highest m/z value. There is also a small peak at M + 1 due to the presence of different isotopes in the molecules. Although ^{12}C is the most abundant carbon isotope, a small amount (1.10% natural abundance) of ^{13}C is also present. Thus, a certain percentage of the molecules analyzed in the mass spectrometer are likely to contain a ^{13}C atom, giving rise to the observed M + 1 peak. In addition, a small amount of ^{2}H (deuterium; 0.015% natural abundance) is present, making a further contribution to the M + 1 peak.

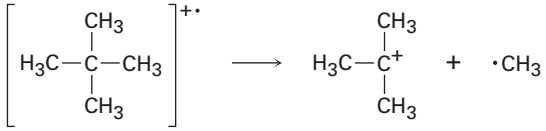
Mass spectrometry would be useful even if molecular weight and formula were the only information that could be obtained, but in fact it provides much more. For one thing, the mass spectrum of a compound serves as a kind of "molecular fingerprint." Each organic compound fragments in a unique way depending on its structure, and the likelihood of two compounds having identical mass spectra is small. Thus, it's sometimes possible to identify an unknown by computer-based matching of its mass spectrum to one of the more than 592,000 spectra recorded in a database called the *Registry of Mass Spectral Data*.

It's also possible to derive structural information about a molecule by interpreting its fragmentation pattern. Fragmentation occurs when the high-energy

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

cation radical flies apart by spontaneous cleavage of a chemical bond. One of the two fragments retains the positive charge and is a carbocation, while the other fragment is a neutral radical.

Not surprisingly, the positive charge often remains with the fragment that is best able to stabilize it. In other words, a relatively stable carbocation is often formed during fragmentation. For example, 2,2-dimethylpropane tends to fragment in such a way that the positive charge remains with the *tert*-butyl group. 2,2-Dimethylpropane therefore has a base peak at $m/z = 57$, corresponding to $C_4H_9^+$ (Figure 12-4).



m/z = 57

Because mass-spectral fragmentation patterns are usually complex, it's often difficult to assign structures to fragment ions. Most hydrocarbons fragment in many ways, as demonstrated by the mass spectrum of hexane in **FIGURE 12-5**. The hexane spectrum shows a moderately abundant molecular ion at $m/z = 86$ and fragment ions at $m/z = 71$, 57, 43, and 29. Since all the carbon–carbon bonds of hexane are electronically similar, all break to a similar extent, giving rise to the observed mixture of ions.

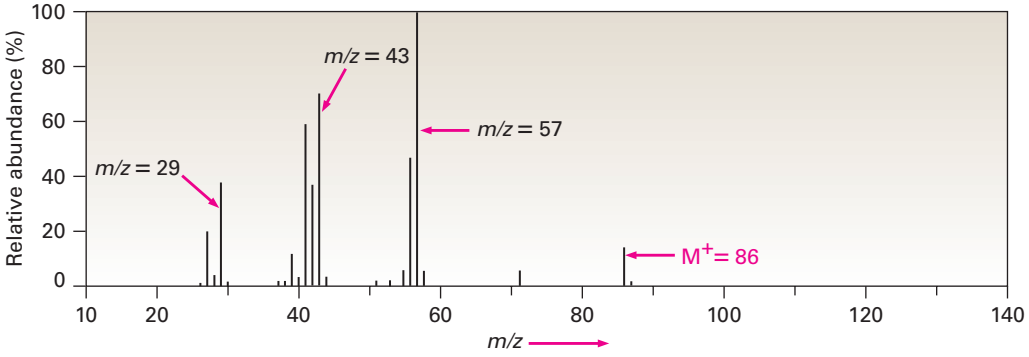
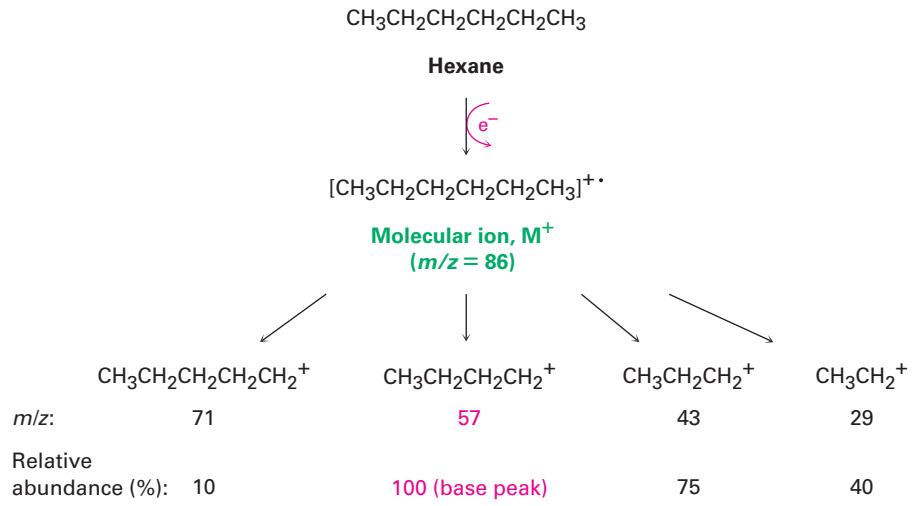


FIGURE 12-5 Mass spectrum of hexane (C_6H_{14}; MW = 86). The base peak is at $m/z = 57$, and numerous other ions are present.

FIGURE 12-6 shows how the hexane fragments might arise. The loss of a methyl radical from the hexane cation radical ($M^+ = 86$) gives rise to a fragment of mass 71; the loss of an ethyl radical accounts for a fragment of mass 57; the loss of a propyl radical accounts for a fragment of mass 43; and the loss of a butyl radical accounts for a fragment of mass 29. With practice, it's sometimes possible to analyze the fragmentation pattern of an unknown compound and work backward to a structure that is compatible with the data.

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

FIGURE 12-6 Fragmentation of hexane in a mass spectrometer.

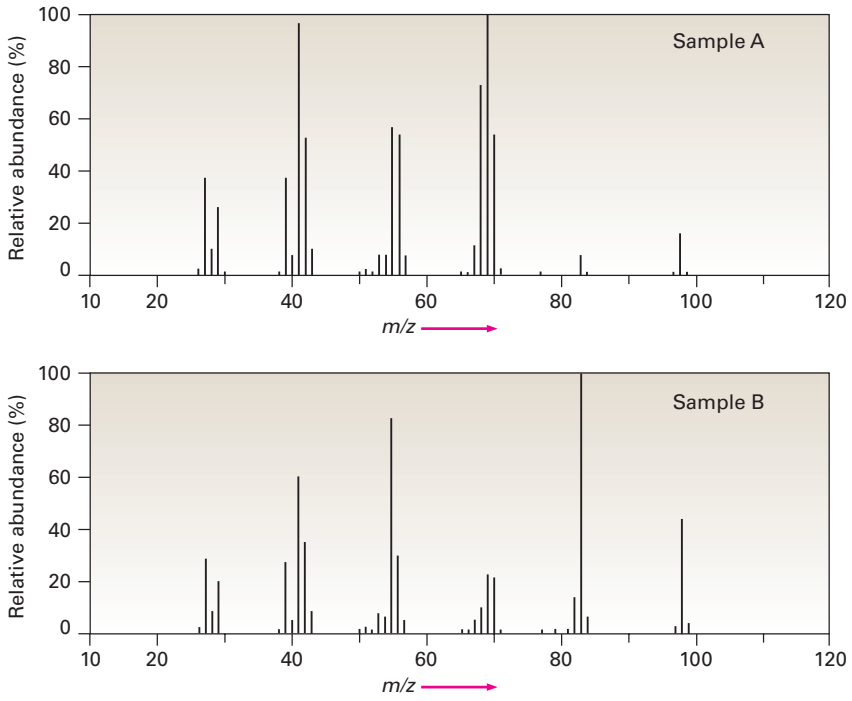


We'll see in the next section and in later chapters that specific functional groups, such as alcohols, ketones, aldehydes, and amines, show specific kinds of mass spectral fragmentations that can be interpreted to provide structural information.

Worked Example 12-1 Using Mass Spectra to Identify Compounds

Assume that you have two unlabeled samples, one of methylcyclohexane and the other of ethylcyclopentane. How could you use mass spectrometry to tell them apart? The mass spectra of both are shown in **FIGURE 12-7**.

FIGURE 12-7 Mass spectra of unlabeled samples **A** and **B** for Worked Example 12-1.



Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Strategy

Look at the possible structures and decide on how they differ. Then think about how any of these differences in structure might give rise to differences in mass spectra. Methylcyclohexane, for instance, has a $-CH_3$ group, and ethylcyclopentane has a $-CH_2CH_3$ group, which should affect the fragmentation patterns.

Solution

Both mass spectra show molecular ions at $M^+ = 98$, corresponding to C_7H_{14}, but they differ in their fragmentation patterns. Sample **A** has its base peak at $m/z = 69$, corresponding to the loss of a CH_2CH_3 group (29 mass units), but **B** has a rather small peak at $m/z = 69$. Sample **B** shows a base peak at $m/z = 83$, corresponding to the loss of a CH_3 group (15 mass units), but sample **A** has only a small peak at $m/z = 83$. We can therefore be reasonably certain that **A** is ethylcyclopentane and **B** is methylcyclohexane.

PROBLEM 12-1

The male sex hormone testosterone contains only C, H, and O and has a mass of 288.2089 amu, as determined by high-resolution mass spectrometry. What is the likely molecular formula of testosterone?

PROBLEM 12-2

Two mass spectra are shown in FIGURE 12-8. One spectrum is that of 2-methyl-2-pentene; the other is of 2-hexene. Which is which? Explain.

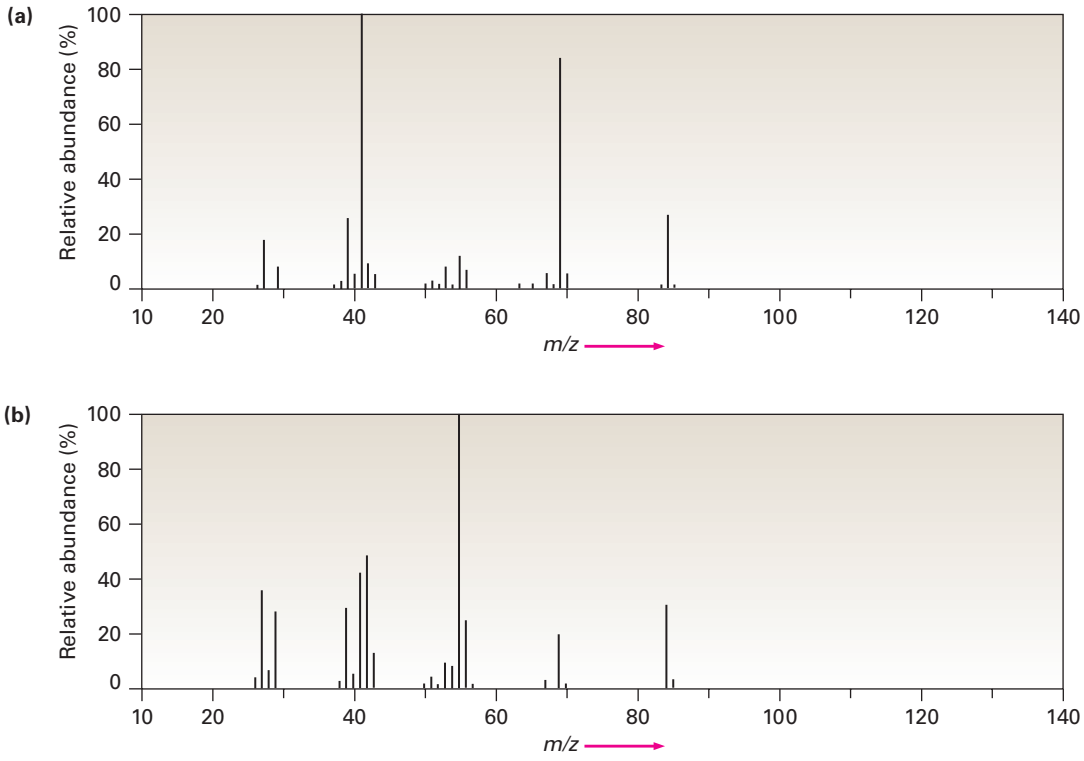


FIGURE 12-8 Mass spectra for Problem 12-2.

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

12-3 Mass Spectrometry of Some Common Functional Groups

As each functional group is discussed in future chapters, mass-spectral fragmentations characteristic of that group will be described. As a preview, though, we'll point out some distinguishing features of several common functional groups.

Alcohols

Alcohols undergo fragmentation in a mass spectrometer by two pathways: *alpha cleavage* and *dehydration*. In the α-cleavage pathway, a C–C bond nearest the hydroxyl group is broken, yielding a neutral radical plus a resonance-stabilized, oxygen-containing cation. This type of fragmentation is seen in the spectrum of 2-pentanol in **FIGURE 12-9**.

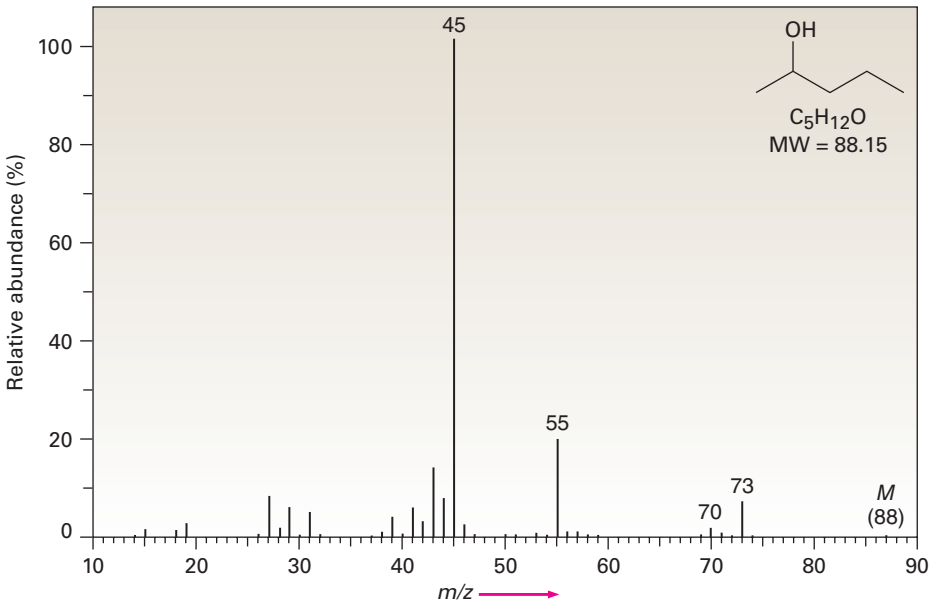
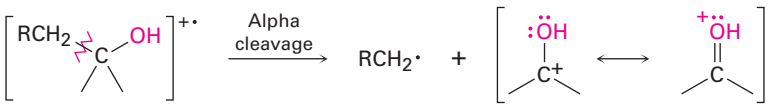
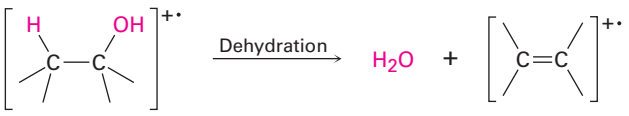


FIGURE 12-9 Mass spectrum of 2-pentanol.



In the dehydration pathway, water is eliminated, yielding an alkene radical cation with a mass 18 units less than M^+. For simplicity, we have drawn the dehydration below as an E2-type process. Often the hydrogen that is lost is not beta to the hydroxyl. Only a small peak from dehydration is observed in the spectrum of 2-pentanol (Figure 12-9).

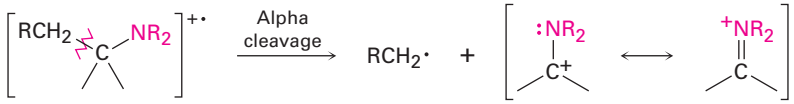


Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Amines

The *nitrogen rule* of mass spectrometry says that a compound with an odd number of nitrogen atoms has an odd-numbered molecular weight. The logic behind the rule comes from the fact that nitrogen is trivalent, thus requiring an odd number of hydrogen atoms. The presence of nitrogen in a molecule is often detected simply by observing its mass spectrum. An odd-numbered molecular ion usually means that the unknown compound has one or three nitrogen atoms, and an even-numbered molecular ion usually means that a compound has either zero or two nitrogen atoms.

Aliphatic amines undergo a characteristic α cleavage in a mass spectrometer, similar to that observed for alcohols. A C–C bond nearest the nitrogen atom is broken, yielding an alkyl radical and a resonance-stabilized, nitrogen-containing cation.



The mass spectrum of triethylamine has a base peak at $m/z = 86$, which arises from an alpha cleavage resulting in the loss of a methyl group **(FIGURE 12-10)**.

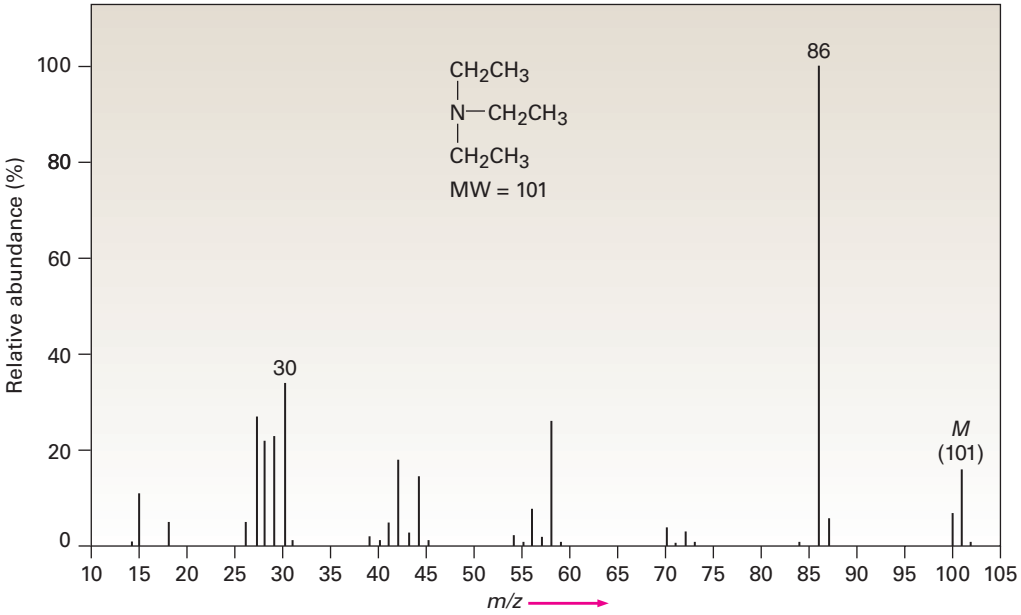


FIGURE 12-10 Mass spectrum of triethylamine.

Halides

The fact that some elements have two common isotopes gives their mass spectra a distinctive appearance. Chlorine, for example, exists as two isotopes, ^{35}Cl and ^{37}Cl, in roughly a 3:1 ratio. In a sample of chloroethane, three out of four molecules contain a ^{35}Cl atom and one out of four has a ^{37}Cl atom. In the mass spectrum of chloroethane **(FIGURE 12-11)**, we see the molecular ion (M) at $m/z = 64$ for ions that contain a ^{35}Cl and another peak at $m/z = 66$, called the M + 2 peak, for ions containing a ^{37}Cl. The ratio of the relative abundance of M:M + 2 is about 3:1, a reflection of the isotopic abundances of chlorine.

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

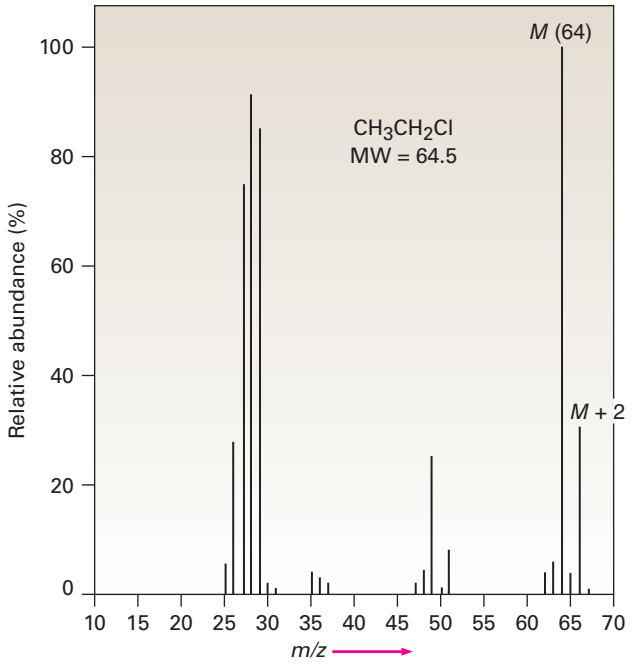


FIGURE 12-11 Mass spectrum of chloroethane.

In the case of bromine, the isotopic distribution is 50.7% ^{79}Br and 49.3% ^{81}Br. In the mass spectrum of 1-bromohexane **(FIGURE 12-12)** the molecular ion appears at $m/z = 164$ for ^{79}Br-containing ions and the M + 2 peak is at $m/z = 166$ for ^{81}Br-containing ions. The ions at $m/z = 135$ and 137 are informative as well. The two nearly equally large peaks tell us that the ions at those m/z values still contain the bromine atom. The peak at $m/z = 85$, on the other hand, does not contain bromine because there is not a large peak at $m/z = 87$.

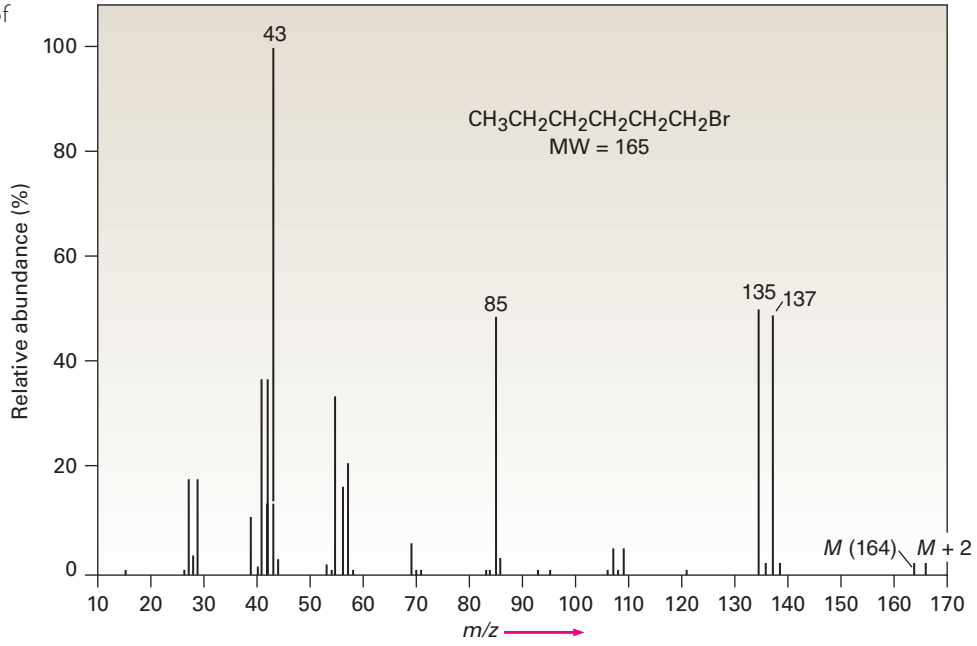
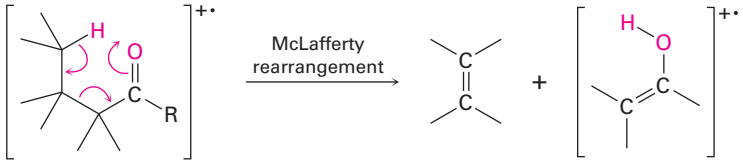


FIGURE 12-12 Mass spectrum of 1-bromohexane.

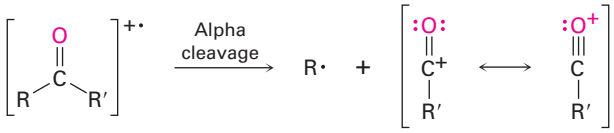
Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Carbonyl Compounds

Ketones and aldehydes that have a hydrogen on a carbon three atoms away from the carbonyl group undergo a characteristic mass-spectral cleavage called the *McLafferty rearrangement.* The hydrogen atom is transferred to the carbonyl oxygen, a C–C bond is broken, and a neutral alkene fragment is produced. The charge remains with the oxygen-containing fragment.



In addition, ketones and aldehydes frequently undergo α cleavage of the bond between the carbonyl group and the neighboring carbon. Alpha cleavage yields a neutral radical and a resonance-stabilized acyl cation.



The mass spectrum of butyrophenone illustrates both alpha cleavage and the McLafferty rearrangement **(FIGURE 12-13)**. Alpha cleavage of the propyl substituent results in the loss of C_3H_7 = 43 mass units from the parent ion at m/z = 148 to give the fragment ion at m/z = 105. A McLafferty rearrangement of butyrophenone results in the loss of ethylene, C_2H_4 = 28 mass units, from the parent leaving the ion at m/z = 120.

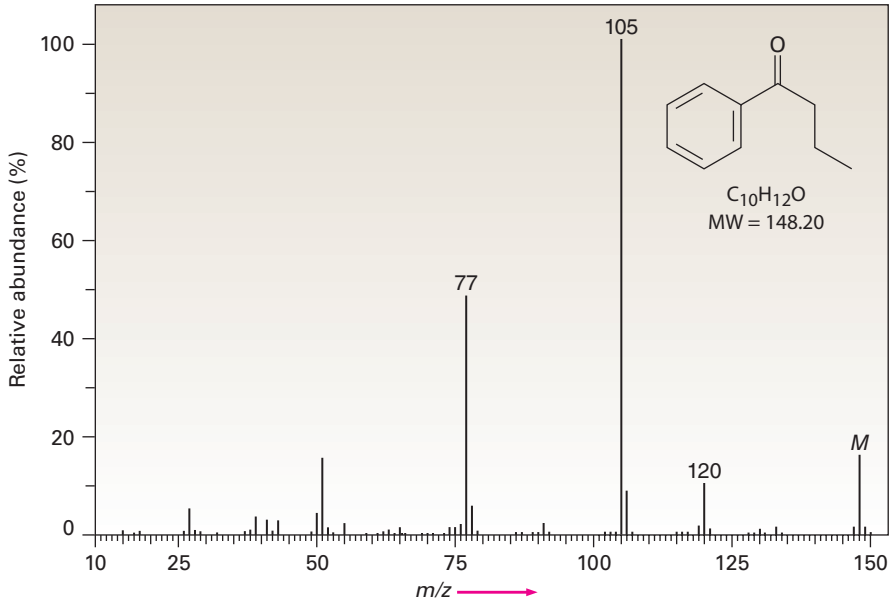


FIGURE 12-13 Mass spectrum of butyrophenone.

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Worked Example 12-2 Identifying Fragmentation Patterns in a Mass Spectrum

The mass spectrum of 2-methyl-3-pentanol is shown in FIGURE 12-14. What fragments can you identify?

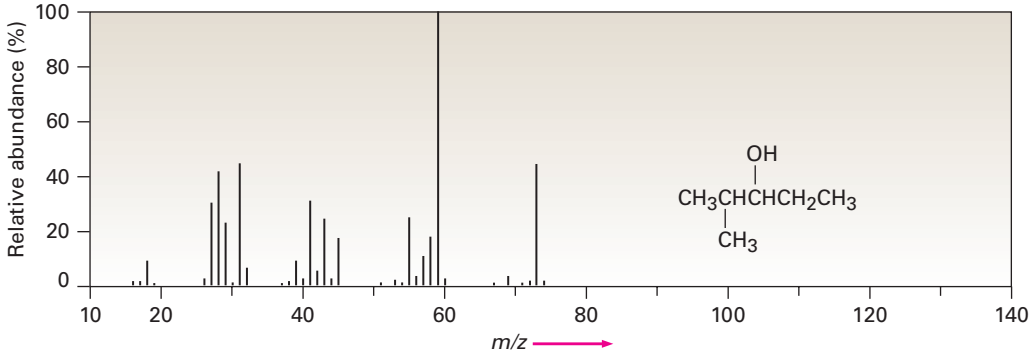


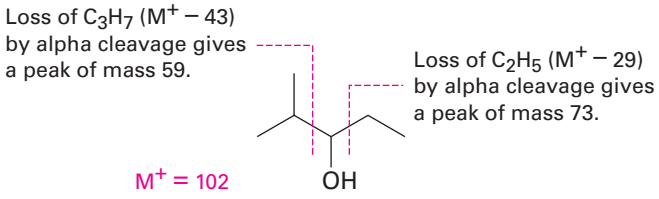
FIGURE 12-14 Mass spectrum of 2-methyl-3-pentanol, Worked Example 12-2.

Strategy

Calculate the mass of the molecular ion, and identify the functional groups in the molecule. Then write the fragmentation processes you might expect, and compare the masses of the resultant fragments with the peaks present in the spectrum.

Solution

2-Methyl-3-pentanol, an open-chain alcohol, has $M^+ = 102$ and might be expected to fragment by α cleavage and by dehydration. These processes would lead to fragment ions of $m/z = 84$, 73, and 59. Of the three expected fragments, dehydration is not observed (no $m/z = 84$ peak), but both α cleavages take place ($m/z = 73$, 59).



PROBLEM 12-3

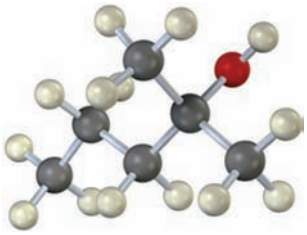
What are the masses of the charged fragments produced in the following cleavage pathways?

(a) Alpha cleavage of 2-pentanone ($CH_3COCH_2CH_2CH_3$)
(b) Dehydration of cyclohexanol (hydroxycyclohexane)
(c) McLafferty rearrangement of 4-methyl-2-pentanone [$CH_3COCH_2CH(CH_3)_2$]
(d) Alpha cleavage of triethylamine [$(CH_3CH_2)_3N$]

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

PROBLEM 12-4

List the masses of the parent ion and of several fragments you might expect to find in the mass spectrum of the following molecule:



12-4 Mass Spectrometry in Biological Chemistry: Time-of-Flight (TOF) Instruments

Most biochemical analyses by MS use either electrospray ionization (*ESI*) or matrix-assisted laser desorption ionization (*MALDI*), typically linked to a time-of-flight (*TOF*) mass analyzer. Both ESI and MALDI are soft ionization methods that produce charged molecules with little fragmentation, even with biological samples of very high molecular weight.

In an ESI source, as a sample solution exits the tube, it is subjected to a high voltage that causes the droplets to become charged. The sample molecules gain one or more protons from charged solvent molecules in the droplet. The volatile solvent quickly evaporates, giving variably protonated sample molecules ($M + H_n^{n+}$). In a MALDI source, the sample is adsorbed onto a suitable matrix compound, such as 2,5-dihydroxybenzoic acid, which is ionized by a short burst of laser light. The matrix compound then transfers the energy to the sample and protonates it, forming $M + H_n^{n+}$ ions.

Following ion formation, the variably protonated sample molecules are electrically focused into a small packet with a narrow spatial distribution, and the packet is given a sudden kick of energy by an accelerator electrode. As each molecule in the packet is given the same energy, $E = mv^2/2$, it begins moving with a velocity that depends on the square root of its mass, $v = \sqrt{2E/m}$. Lighter molecules move faster, and heavier molecules move slower. The analyzer itself—the *drift tube*—is simply an electrically grounded metal tube inside which the different charged molecules become separated as they move at different velocities and take different amounts of time to complete their flight.

The TOF technique is considerably more sensitive than the magnetic sector alternative, and protein samples of up to 100 kilodaltons (100,000 amu) can be separated with a mass accuracy of 3 ppm. **FIGURE 12-15** shows a MALDI–TOF spectrum of chicken egg-white lysozyme, MW = 14,306.7578 daltons. Biochemists generally use the unit *dalton,* abbreviated Da, instead of amu, although the two are equivalent (1 dalton = 1 amu).

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

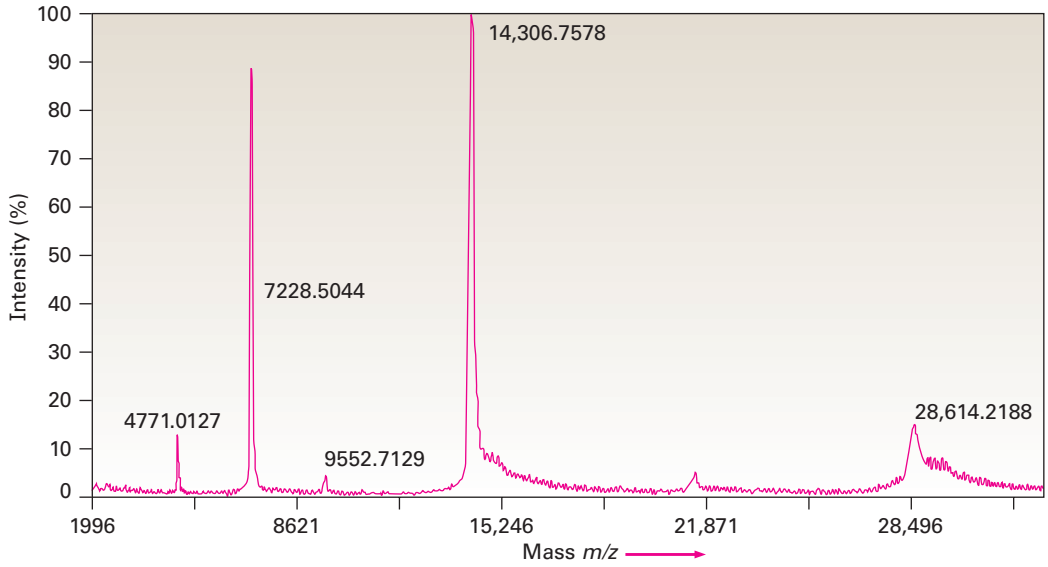


FIGURE 12-15 MALDI–TOF mass spectrum of chicken egg-white lysozyme. The peak at 14,306.7578 daltons (amu) is due to the monoprotonated protein, $M+H^+$, and the peak at 28,614.2188 daltons is due to an impurity formed by dimerization of the protein. Other peaks at lower m/z values are various protonated species, $M+H_n^{n+}$.

12-5 Spectroscopy and the Electromagnetic Spectrum

Infrared, ultraviolet, and nuclear magnetic resonance spectroscopies differ from mass spectrometry in that they are nondestructive and involve the interaction of molecules with electromagnetic energy rather than with an ionizing source. Before beginning a study of these techniques, however, let's briefly review the nature of radiant energy and the electromagnetic spectrum.

Visible light, X rays, microwaves, radio waves, and so forth are all different kinds of *electromagnetic radiation*. Collectively, they make up the **electromagnetic spectrum**, shown in FIGURE 12-16. The electromagnetic spectrum is arbitrarily divided into regions, with the familiar visible region accounting for only a small portion, from 3.8×10^{-7} m to 7.8×10^{-7} m in wavelength. The visible region is flanked by the infrared and ultraviolet regions.

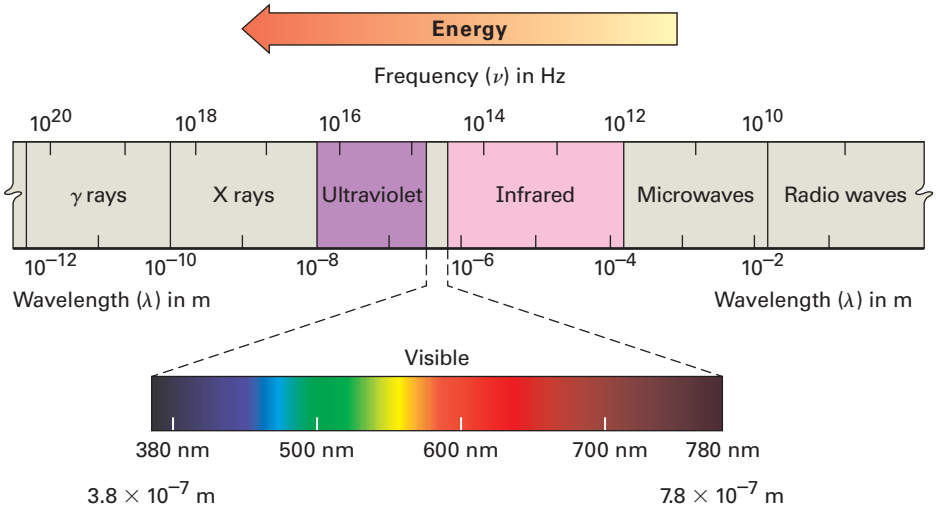


FIGURE 12-16 The electromagnetic spectrum covers a continuous range of wavelengths and frequencies, from radio waves at the low-frequency end to gamma (γ) rays at the high-frequency end. The familiar visible region accounts for only a small portion near the middle of the spectrum.

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Electromagnetic radiation is often said to have dual behavior. In some respects, it has the properties of a particle, called a *photon,* yet in other respects it behaves as an energy wave. Like all waves, electromagnetic radiation is characterized by a *wavelength,* a *frequency,* and an *amplitude* (FIGURE 12-17). The **wavelength, λ** (Greek lambda), is the distance from one wave maximum to the next. The **frequency, ν** (Greek nu), is the number of waves that pass by a fixed point per unit time, usually given in reciprocal seconds (s^{-1}), or **hertz, Hz** (1 Hz = 1 s^{-1}). The **amplitude** is the height of a wave, measured from midpoint to peak. The intensity of radiant energy, whether a feeble glow or a blinding glare, is proportional to the square of the wave's amplitude.

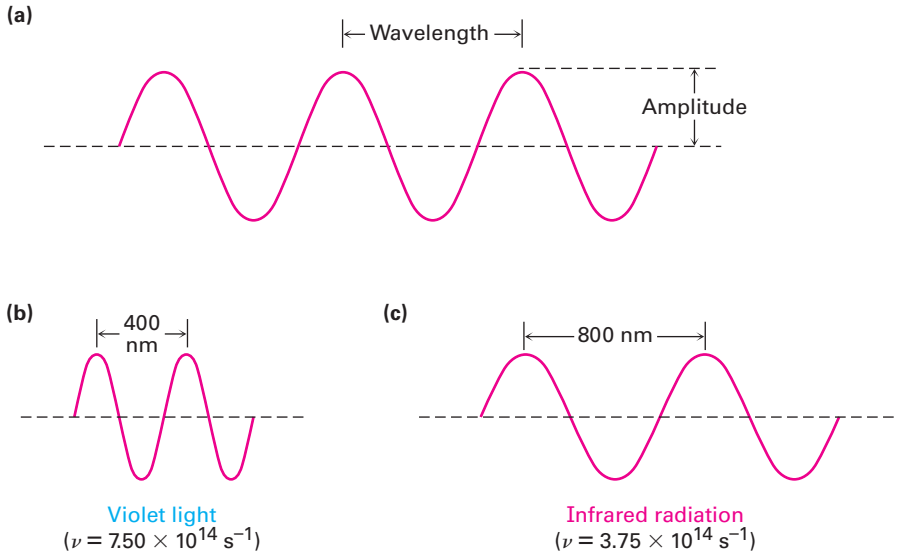


FIGURE 12-17 Electromagnetic waves are characterized by a wavelength, a frequency, and an amplitude. **(a)** Wavelength (λ) is the distance between two successive wave maxima. Amplitude is the height of the wave measured from the center. **(b)–(c)** What we perceive as different kinds of electromagnetic radiation are simply waves with different wavelengths and frequencies.

Multiplying the wavelength of a wave in meters (m) by its frequency in reciprocal seconds (s^{-1}) gives the speed of the wave in meters per second (m/s). The rate of travel of all electromagnetic radiation in a vacuum is a constant value, commonly called the "speed of light" and abbreviated *c.* Its numerical value is defined as exactly 2.997 924 58 $\times 10^8$ m/s, usually rounded off to 3.00 $\times 10^8$ m/s.

$$\text{Wavelength} \times \text{Frequency} = \text{Speed}$$

$$\lambda\ (\text{m}) \times \nu\ (\text{s}^{-1}) = c\ (\text{m/s})$$

$$\lambda = \frac{c}{\nu} \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

Just as matter comes only in discrete units called atoms, electromagnetic energy is transmitted only in discrete amounts called *quanta.* The amount of energy ε corresponding to 1 quantum of energy (1 photon) of a given frequency ν is expressed by the Planck equation

$$\varepsilon = h\nu = \frac{hc}{\lambda}$$

where h = Planck's constant (6.62×10^{-34} J · s = 1.58×10^{-34} cal · s).

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

The Planck equation says that the energy of a given photon varies directly with its frequency ν but inversely with its wavelength λ. High frequencies and short wavelengths correspond to high-energy radiation such as gamma rays; low frequencies and long wavelengths correspond to low-energy radiation such as radio waves. Multiplying ε by Avogadro's number N_A gives the same equation in more familiar units, where E represents the energy of Avogadro's number (one "mole") of photons of wavelength λ:

$$E = \frac{N_A hc}{\lambda} = \frac{1.20 \times 10^{-4}\ \text{kJ/mol}}{\lambda\ (\text{m})} \quad \text{or} \quad \frac{2.86 \times 10^{-5}\ \text{kcal/mol}}{\lambda\ (\text{m})}$$

When an organic compound is exposed to a beam of electromagnetic radiation, it absorbs energy of some wavelengths but passes, or transmits, energy of other wavelengths. If we irradiate the sample with energy of many different wavelengths and determine which are absorbed and which are transmitted, we can measure the **absorption spectrum** of the compound.

An example of an absorption spectrum—that of ethanol exposed to infrared radiation—is shown in FIGURE 12-18. The horizontal axis records the wavelength, and the vertical axis records the intensity of the various energy absorptions in percent transmittance. The baseline corresponding to 0% absorption (or 100% transmittance) runs along the top of the chart, so a downward spike means that energy absorption has occurred at that wavelength.

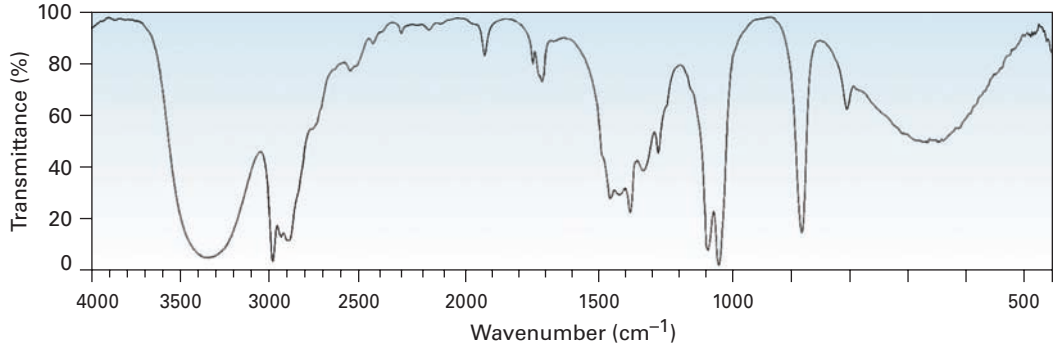


FIGURE 12-18 An infrared absorption spectrum for ethanol, CH_3CH_2OH. A transmittance of 100% means that all the energy is passing through the sample, whereas a lower transmittance means that some energy is being absorbed. Thus, each downward spike corresponds to an energy absorption.

The energy a molecule gains when it absorbs radiation must be distributed over the molecule in some way. With infrared radiation, the absorbed energy causes bonds to stretch and bend more vigorously. With ultraviolet radiation, the energy causes an electron to jump from a lower-energy orbital to a higher-energy one. Different radiation frequencies affect molecules in different ways, but each provides structural information when the results are interpreted.

There are many kinds of spectroscopies, which differ according to the region of the electromagnetic spectrum used. We'll look at three: infrared spectroscopy, ultraviolet spectroscopy, and nuclear magnetic resonance spectroscopy. Let's begin by seeing what happens when an organic sample absorbs infrared energy.

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Correlating Energy and Frequency of Radiation — Worked Example 12-3

Which is higher in energy, FM radio waves with a frequency of 1.015×10^8 Hz (101.5 MHz) or visible green light with a frequency of 5×10^{14} Hz?

Strategy

Remember the equations $\varepsilon = h\nu$ and $\varepsilon = hc/\lambda$, which say that energy increases as frequency increases and as wavelength decreases.

Solution

Since visible light has a higher frequency than radio waves, it is higher in energy.

PROBLEM 12-5

Which has higher energy, infrared radiation with $\lambda = 1.0 \times 10^{-6}$ m or an X ray with $\lambda = 3.0 \times 10^{-9}$ m? Radiation with $\nu = 4.0 \times 10^9$ Hz or with $\lambda = 9.0 \times 10^{-6}$ m?

PROBLEM 12-6

It's useful to develop a feeling for the amounts of energy that correspond to different parts of the electromagnetic spectrum. Calculate the energies in kJ/mol of each of the following kinds of radiation:

(a) A gamma ray with $\lambda = 5.0 \times 10^{-11}$ m
(b) An X ray with $\lambda = 3.0 \times 10^{-9}$ m
(c) Ultraviolet light with $\nu = 6.0 \times 10^{15}$ Hz
(d) Visible light with $\nu = 7.0 \times 10^{14}$ Hz
(e) Infrared radiation with $\lambda = 2.0 \times 10^{-5}$ m
(f) Microwave radiation with $\nu = 1.0 \times 10^{11}$ Hz

12-6 Infrared Spectroscopy

In **infrared (IR) spectroscopy**, the IR region of the electromagnetic spectrum covers the range from just above the visible (7.8×10^{-7} m) to approximately 10^{-4} m, but only the midportion from 2.5×10^{-6} m to 2.5×10^{-5} m is used by organic chemists (FIGURE 12-19). Wavelengths within the IR region are usually given in micrometers ($1\ \mu\text{m} = 10^{-6}$ m), and frequencies are given in wavenumbers rather than in hertz. The **wavenumber** $\tilde{\nu}$ is the reciprocal of wavelength in centimeters and is therefore expressed in units of cm^{-1}.

$$\text{Wavenumber:} \quad \tilde{\nu}\ (\text{cm}^{-1}) = \frac{1}{\lambda\ (\text{cm})}$$

Thus, the useful IR region is from 4000 to 400 cm^{-1}, corresponding to energies of 48.0 kJ/mol to 4.80 kJ/mol (11.5–1.15 kcal/mol).

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

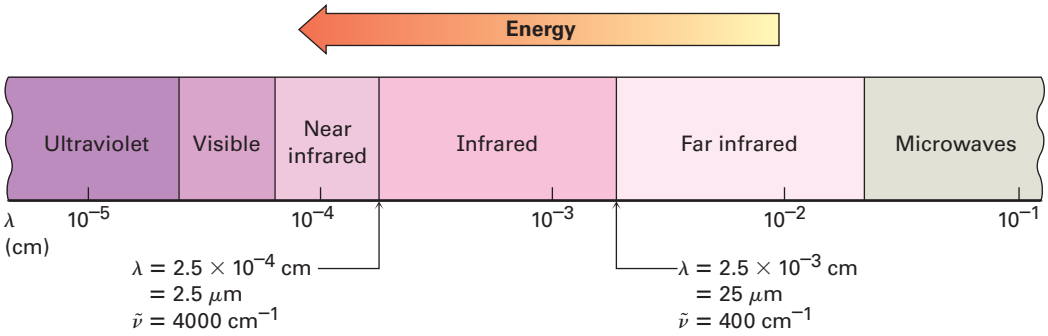
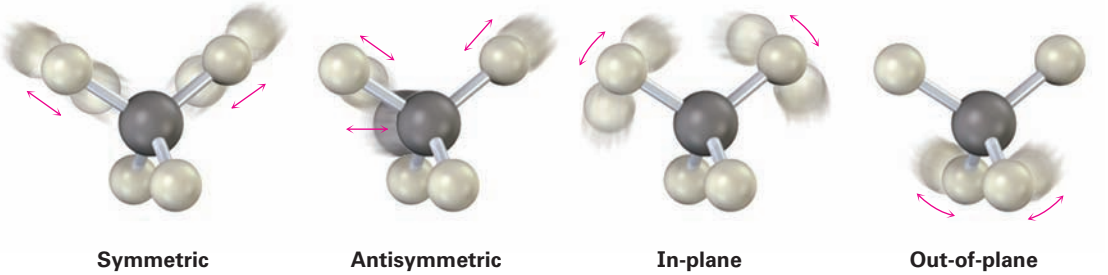


FIGURE 12-19 The infrared and adjacent regions of the electromagnetic spectrum.

Why does an organic molecule absorb some wavelengths of IR radiation but not others? All molecules have a certain amount of energy and are in constant motion. Their bonds stretch and contract, atoms wag back and forth, and other molecular vibrations occur. Some of the kinds of allowed vibrations are shown below:



Symmetric stretching | **Antisymmetric stretching** | **In-plane bending** | **Out-of-plane bending**

The amount of energy a molecule contains is not continuously variable but is *quantized*. That is, a molecule can stretch or bend only at specific frequencies corresponding to specific energy levels. Take bond stretching, for example. Although we usually speak of bond lengths as if they were fixed, the numbers given are really averages. In fact, a typical C–H bond with an average bond length of 110 pm is actually vibrating at a specific frequency, alternately stretching and contracting as if there were a spring connecting the two atoms.

When a molecule is irradiated with electromagnetic radiation, energy is absorbed if the frequency of the radiation matches the frequency of the vibration. The result of this energy absorption is an increased amplitude for the vibration; in other words, the "spring" connecting the two atoms stretches and compresses a bit further. Since each frequency absorbed by a molecule corresponds to a specific molecular motion, we can find what kinds of motions a molecule has by measuring its IR spectrum. By interpreting these motions, we can find out what kinds of bonds (functional groups) are present in the molecule.

IR spectrum → What molecular motions? → What functional groups?

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

12-7 Interpreting Infrared Spectra

The complete interpretation of an IR spectrum is difficult because most organic molecules have dozens of different bond stretching and bending motions, and thus have dozens of absorptions. On the one hand, this complexity is a problem because it generally limits the laboratory use of IR spectroscopy to pure samples of fairly small molecules—little can be learned from IR spectroscopy about large, complex biomolecules. On the other hand, this complexity is useful because an IR spectrum acts as a unique fingerprint of a compound. In fact, the complex region of the IR spectrum, from 1500 cm^{-1} to around 400 cm^{-1}, is called the *fingerprint region.* If two samples have identical IR spectra, they are almost certainly identical compounds.

Fortunately, we don't need to interpret an IR spectrum fully to get useful structural information. Most functional groups have characteristic IR absorption bands that don't change much from one compound to another. The C=O absorption of a ketone is almost always in the range 1680 to 1750 cm^{-1}; the O–H absorption of an alcohol is almost always in the range 3400 to 3650 cm^{-1}; the C=C absorption of an alkene is almost always in the range 1640 to 1680 cm^{-1}; and so forth. By learning where characteristic functional-group absorptions occur, it's possible to get structural information from IR spectra. TABLE 12-1 lists the characteristic IR bands of some common functional groups.

TABLE 12-1 Characteristic IR Absorptions of Some Functional Groups

Functional Group	Absorption (cm^{-1})	Intensity	Functional Group	Absorption (cm^{-1})	Intensity
Alkane			Amine		
C–H	2850–2960	Medium	N–H	3300–3500	Medium
Alkene			C–N	1030–1230	Medium
=C–H	3020–3100	Medium	Carbonyl compound		
C=C	1640–1680	Medium	C=O	1670–1780	Strong
Alkyne			Aldehyde	1730	Strong
≡C–H	3300	Strong	Ketone	1715	Strong
C≡C	2100–2260	Medium	Ester	1735	Strong
Alkyl halide			Amide	1690	Strong
C–Cl	600–800	Strong	Carboxylic acid	1710	Strong
C–Br	500–600	Strong	Carboxylic acid		
Alcohol			O–H	2500–3100	Strong, broad
O–H	3400–3650	Strong, broad	Nitrile		
C–O	1050–1150	Strong	C≡N	2210–2260	Medium
Arene			Nitro		
C–H	3030	Weak	NO_2	1540	Strong
Aromatic ring	1660–2000	Weak			
	1450–1600	Medium			

Look at the IR spectra of hexane, 1-hexene, and 1-hexyne in FIGURE 12-20 to see an example of how IR spectroscopy can be used. Although all three IR

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

spectra contain many peaks, there are characteristic absorptions of C=C and C≡C functional groups that allow the three compounds to be distinguished. Thus, 1-hexene shows a characteristic C=C absorption at 1660 cm^{-1} and a vinylic =C–H absorption at 3100 cm^{-1}, whereas 1-hexyne has a C≡C absorption at 2100 cm^{-1} and a terminal alkyne ≡C–H absorption at 3300 cm^{-1}.

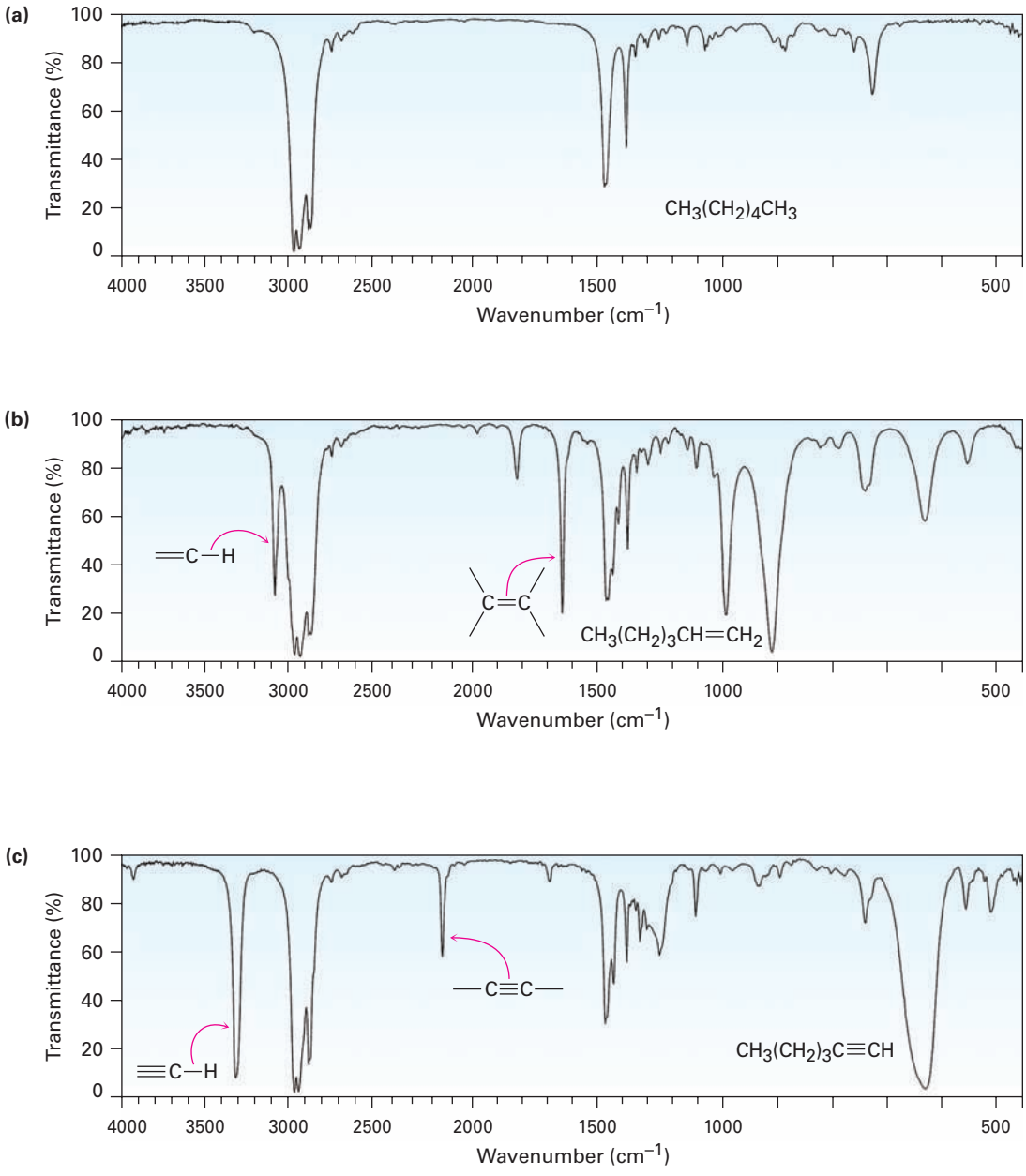


FIGURE 12-20 IR spectra of **(a)** hexane, **(b)** 1-hexene, and **(c)** 1-hexyne. Spectra like these are easily obtained from submilligram amounts of material in a few minutes using commercially available instruments.

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

It helps in remembering the position of specific IR absorptions to divide the IR region from 4000 cm^{-1} to 400 cm^{-1} into four parts, as shown in **FIGURE 12-21**.

- The region from 4000 to 2500 cm^{-1} corresponds to absorptions caused by N–H, C–H, and O–H single-bond stretching motions. N–H and O–H bonds absorb in the 3300 to 3600 cm^{-1} range; C–H bond stretching occurs near 3000 cm^{-1}.
- The region from 2500 to 2000 cm^{-1} is where triple-bond stretching occurs. Both C≡N and C≡C bonds absorb here.
- The region from 2000 to 1500 cm^{-1} is where double bonds (C=O, C=N, and C=C) absorb. Carbonyl groups generally absorb in the range 1680 to 1750 cm^{-1}, and alkene stretching normally occurs in the narrow range of 1640 to 1680 cm^{-1}.
- The region below 1500 cm^{-1} is the fingerprint portion of the IR spectrum. A large number of absorptions due to a variety of C–C, C–O, C–N, and C–X single-bond vibrations occur here.

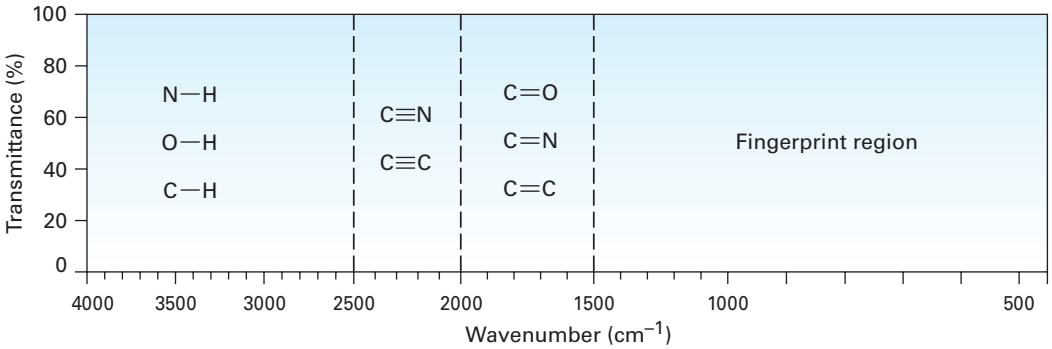


FIGURE 12-21 The four regions of the infrared spectrum: single bonds to hydrogen, triple bonds, double bonds, and fingerprint.

Why do different functional groups absorb where they do? As noted previously, a good analogy is that of two weights (atoms) connected by a spring (a bond). This type of system is a harmonic oscillator. In a harmonic oscillator, when a bond vibrates, its energy of vibration is continually and periodically changing from kinetic to potential energy and back again. The total amount of energy is proportional to the frequency of the vibration,

$$E_{osc} \propto h\nu_{osc}$$

The vibrational frequency of a harmonic oscillator is inversely proportional to the reduced mass of the oscillator, μ, and is directly proportional to the stiffness (strength) of the spring, K. The natural frequency of vibration of a bond is given by the equation

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

Springs connecting small weights vibrate faster than springs connecting large weights. Short, strong bonds vibrate at a higher energy and higher frequency

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

than do long, weak bonds, just as a short, strong spring vibrates faster than a long, weak spring. Thus, triple bonds absorb at a higher frequency than double bonds, which in turn absorb at a higher frequency than single bonds. In addition, C–H, O–H, and N–H bonds vibrate at a higher frequency than bonds between heavier C, O, and N atoms.

C≡C	C=C	C—C
2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

← Increasing K

Worked Example 12-4 **Distinguishing Isomeric Compounds by IR Spectroscopy**

Acetone (CH_3COCH_3) and 2-propen-1-ol ($H_2C{=}CHCH_2OH$) are isomers. How could you distinguish them by IR spectroscopy?

Strategy

Identify the functional groups in each molecule, and refer to Table 12-1.

Solution

Acetone has a strong C=O absorption at 1715 cm^{-1}, while 2-propen-1-ol has an –OH absorption at 3500 cm^{-1} and a C=C absorption at 1660 cm^{-1}.

PROBLEM 12-7

What functional groups might the following molecules contain?

(a) A compound with a strong absorption at 1710 cm^{-1}
(b) A compound with a strong absorption at 1540 cm^{-1}
(c) A compound with strong absorptions at 1720 cm^{-1} and 2500 to 3100 cm^{-1}

PROBLEM 12-8

How might you use IR spectroscopy to distinguish between the following pairs of isomers?

(a) CH_3CH_2OH and CH_3OCH_3 **(b)** Cyclohexane and 1-hexene
(c) $CH_3CH_2CO_2H$ and $HOCH_2CH_2CHO$

12-8 Infrared Spectra of Some Common Functional Groups

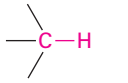
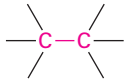
As each functional group is discussed in future chapters, the spectroscopic properties of that group will be described. For the present, we'll point out some distinguishing features of the hydrocarbon functional groups already studied and briefly preview some other common functional groups. We should

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

also point out, however, that in addition to interpreting absorptions that *are* present in an IR spectrum, it's also possible to get structural information by noticing which absorptions are *not* present. If the spectrum of a compound has no absorptions at 3300 and 2150 cm^{-1}, the compound is not a terminal alkyne; if the spectrum has no absorption near 3400 cm^{-1}, the compound is not an alcohol; and so on.

Alkanes

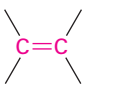
The IR spectrum of an alkane is fairly uninformative because no functional groups are present and all absorptions are due to C–H and C–C bonds. Alkane C–H bonds show a strong absorption from 2850 to 2960 cm^{-1}, and saturated C–C bonds show a number of bands in the 800 to 1300 cm^{-1} range. Since most organic compounds contain saturated alkane-like portions, most organic compounds have these characteristic IR absorptions. The C–H and C–C bands are clearly visible in the three spectra shown in Figure 12-20.

Alkanes		2850–2960 cm^{-1}
		800–1300 cm^{-1}

Alkenes

Alkenes show several characteristic stretching absorptions. Vinylic =C–H bonds absorb from 3020 to 3100 cm^{-1}, and alkene C=C bonds usually absorb near 1650 cm^{-1}, although in some cases their peaks can be rather small and difficult to see clearly when the alkene is symmetric, or nearly so. Both absorptions are visible in the 1-hexene spectrum in Figure 12-20b.

Alkenes have characteristic =C–H out-of-plane bending absorptions in the 700 to 1000 cm^{-1} range, thereby allowing the substitution pattern on a double bond to be determined **(FIGURE 12-22)**. For example, monosubstituted alkenes such as 1-hexene show strong characteristic bands at 910 and 990 cm^{-1}, and 1,1-disubstituted alkenes ($R_2C{=}CH_2$) have an intense band at 890 cm^{-1}.

Alkenes		3020–3100 cm^{-1}
		1640–1680 cm^{-1}
	$RCH{=}CH_2$	910 and 990 cm^{-1}
	$R_2C{=}CH_2$	890 cm^{-1}

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

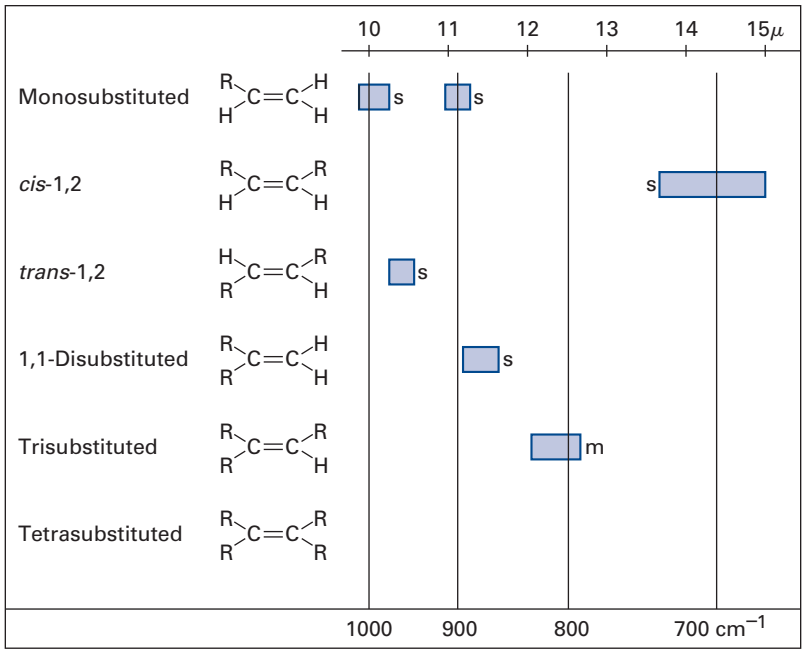


FIGURE 12-22 C–H out-of-plane bending vibrations for substituted alkenes.

Alkynes

Alkynes show a C≡C stretching absorption at 2100 to 2260 cm^{-1}, an absorption that is much more intense for terminal alkynes than for internal alkynes. In fact, symmetrically substituted triple bonds like that in 3-hexyne show no absorption at all, due to the fact that the stretching of a symmetric C≡C bond results in no change of the dipole moment, and no IR radiation is absorbed at that frequency. Terminal alkynes such as 1-hexyne also have a characteristic ≡C–H stretching absorption at 3300 cm^{-1} (Figure 12-20c). This band is diagnostic for terminal alkynes because it is fairly intense and quite sharp.

Alkynes	—C≡C—	2100–2260 cm^{-1}
	≡C—H	3300 cm^{-1}

Aromatic Compounds

Aromatic compounds, such as benzene, have a weak C–H stretching absorption at 3030 cm^{-1}, just to the left of a typical saturated C–H band. In addition, they have a series of weak absorptions in the 1660 to 2000 cm^{-1} range and a series of medium-intensity absorptions in the 1450 to 1600 cm^{-1} region. These latter absorptions are due to complex molecular motions of the entire ring. The C–H out-of-plane bending region for benzene derivatives, between

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

650 to 1000 cm^{-1}, gives valuable information about the ring's substitution pattern, as it does for the substitution pattern of alkenes.

Aromatic compounds		3030 cm^{-1} (weak)
		1660–2000 cm^{-1} (weak) 1450–1600 cm^{-1} (medium)

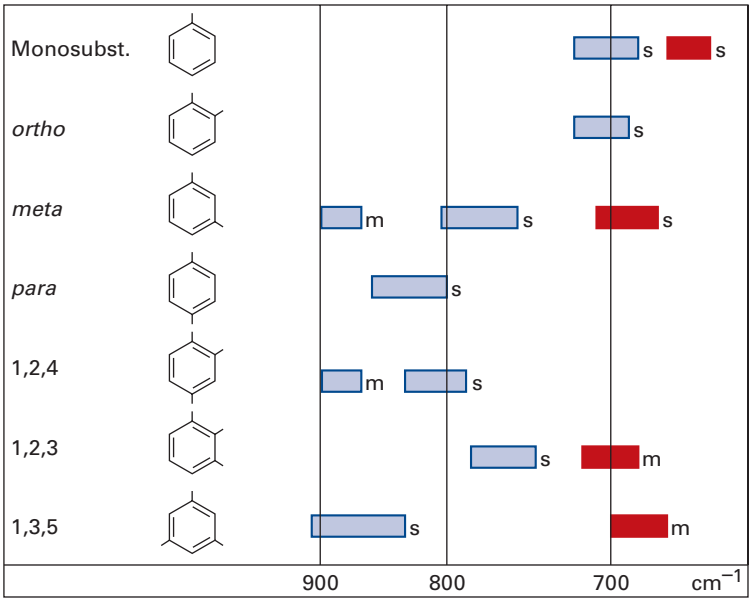


FIGURE 12-23 C–H out-of-plane bending vibrations for substituted benzenes.

The IR spectrum of phenylacetylene, shown in Figure 12-28 at the end of this section, gives an example, clearly showing the following absorbances: ≡C–H stretch at 3300 cm^{-1}, C–H stretches from the benzene ring at 3000 to 3100 cm^{-1}, C=C stretches of the benzene ring between 1450 and 1600 cm^{-1}, and out-of-plane bending of the ring's C–H groups, indicating monosubstitution at 750 cm^{-1}.

Alcohols

The O–H functional group of alcohols is easy to spot. Alcohols have a characteristic band in the range 3400 to 3650 cm^{-1} that is usually broad and intense. Hydrogen bonding between O–H groups is responsible for making the absorbance so broad. If an O–H stretch is present, it's hard to miss this band or to confuse it with anything else.

Alcohols	—O—H	3400–3650 cm^{-1} (broad, intense)

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Cyclohexanol **(FIGURE 12-24)** makes a nice example.

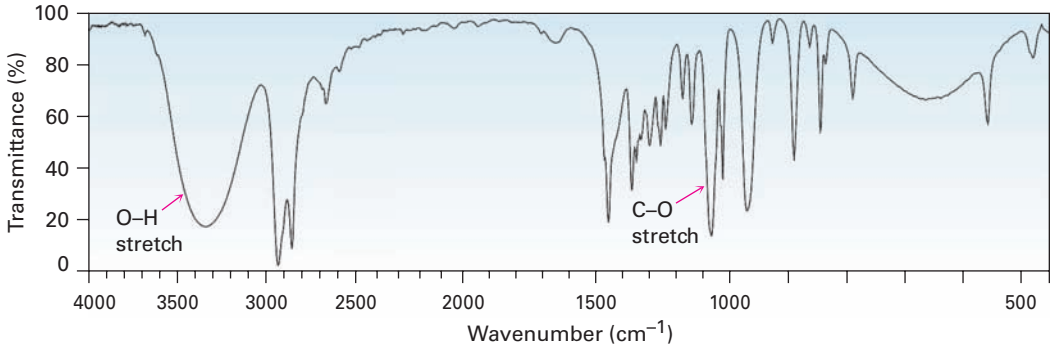


FIGURE 12-24 IR spectrum of cyclohexanol.

Amines

The N–H functional group of amines is also easy to spot in the IR, with a characteristic absorption in the 3300 to 3500 cm^{-1} range. Although alcohols absorb in the same range, an N–H absorption band is much sharper and less intense than an O–H band.

Amines —N—H 3300–3500 cm^{-1} (sharp, medium intensity)

Primary amines exhibit two absorbances—one for the symmetric stretching mode and one for the asymmetric mode **(FIGURE 12-25)**. Secondary amines only have one N–H stretching absorbance in this region.

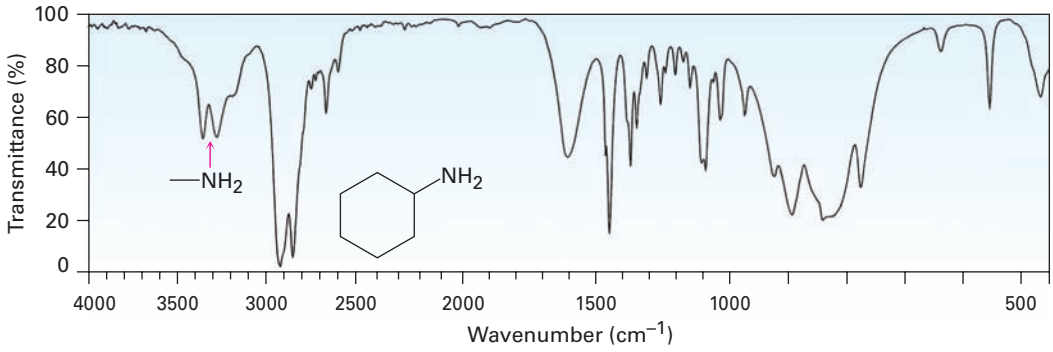


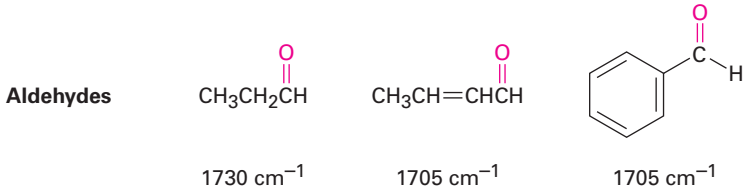
FIGURE 12-25 IR spectrum of cyclohexylamine.

Carbonyl Compounds

Carbonyl functional groups are the easiest to identify of all IR absorptions because of their sharp, intense peak in the range 1670 to 1780 cm^{-1}. Most important, the exact position of absorption within this range can often be used to identify the exact kind of carbonyl functional group—aldehyde, ketone, ester, and so forth. The principles of resonance, inductive electronic effects, and hydrogen bonding help us explain and understand the different frequencies at which different carbonyl groups absorb IR radiation.

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

ALDEHYDES Saturated aldehydes absorb at 1730 cm^{-1}; aldehydes next to either a double bond or an aromatic ring absorb at 1705 cm^{-1}. The lower frequency of absorbance can be explained by resonance delocalization of electron density from the C=C into the carbonyl. This lengthens the C=O slightly, and results in a lower vibrational frequency of the group.



The C–H group attached to the carbonyl is responsible for the characteristic IR absorbance for aldehydes at 2750 and 2850 cm^{-1} **(FIGURE 12-26)**. Although these are not very intense, the absorbance at 2750 cm^{-1} in particular is helpful when trying to distinguish between an aldehyde and a ketone.

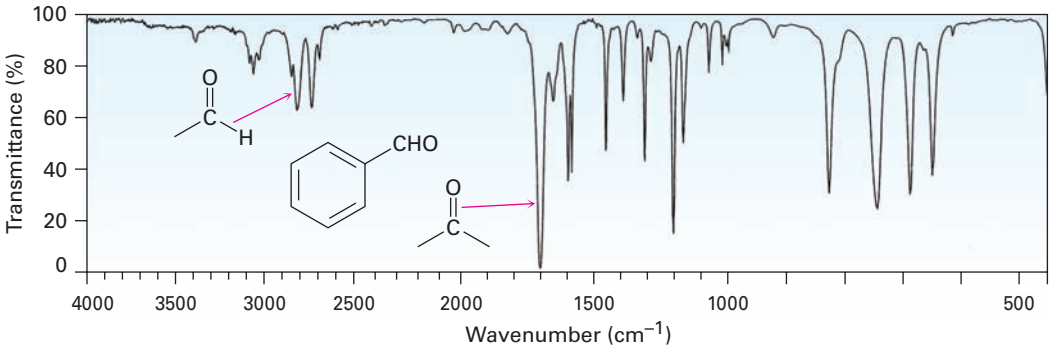
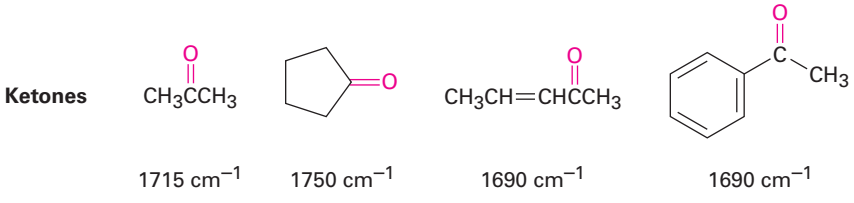


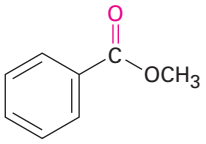
FIGURE 12-26 The IR spectrum of benzaldehyde.

KETONES Saturated open-chain ketones and six-membered cyclic ketones absorb at 1715 cm^{-1}. Ring strain stiffens the C=O bond, making five-membered cyclic ketones absorb at 1750 cm^{-1} and four-membered cyclic ketones absorb at 1780 cm^{-1}. Ketones next to a double bond or an aromatic ring absorb at 1690 cm^{-1}. As with an aldehyde, resonance delocalization of pi-electron density weakens the C=O a bit, causing it to absorb at a lower frequency. As a general rule, a conjugated carbonyl group absorbs IR radiation 20 to 30 cm^{-1} lower than the corresponding saturated carbonyl compound.



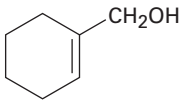
ESTERS Saturated esters absorb at 1735 cm^{-1}. In addition to the C=O absorbance, esters also have two strong absorbances in the 1300 to 1000 cm^{-1} range from the C–O portion of the functional group. Like the other carbonyl functional groups, esters next to either an aromatic ring or a double bond absorb at 1715 cm^{-1}, 20 to 30 cm^{-1} lower than a saturated ester.

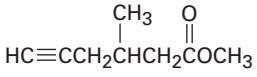
Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Esters	CH_3COCH_3	$CH_3CH{=}CHCOCH_3$	
	1735 cm^{-1}	1715 cm^{-1}	1715 cm^{-1}

Worked Example 12-5 Predicting IR Absorptions of Compounds

Where might the following compounds have IR absorptions?

(a) 

(b) 

Strategy

Identify the functional groups in each molecule, and then check Table 12-1 to see where those groups absorb.

Solution

(a) *Absorptions:* 3400 to 3650 cm^{-1} (O–H), 3020 to 3100 cm^{-1} (=C–H), 1640 to 1680 cm^{-1} (C=C). This molecule has an alcohol O–H group and an alkene double bond.

(b) *Absorptions:* 3300 cm^{-1} (≡C–H), 2100 to 2260 cm^{-1} (C≡C), 1735 cm^{-1} (C=O). This molecule has a terminal alkyne triple bond and a saturated ester carbonyl group.

Worked Example 12-6 Identifying Functional Groups from an IR Spectrum

The IR spectrum of an unknown compound is shown in **FIGURE 12-27**. What functional groups does the compound contain?

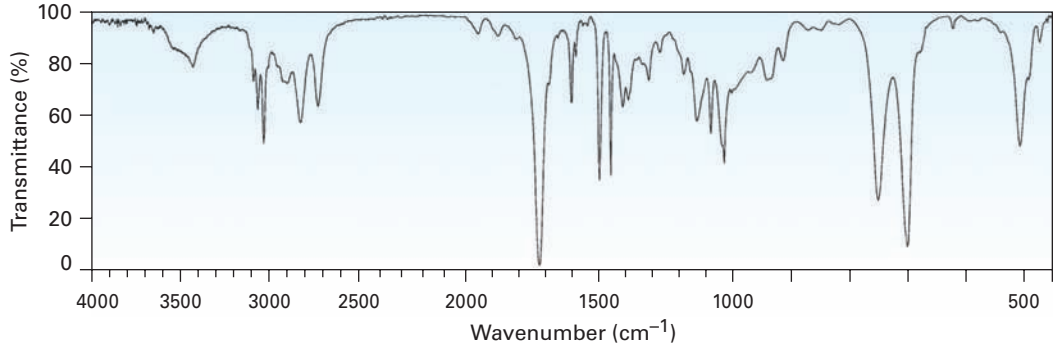


FIGURE 12-27 IR spectrum for Worked Example 12-6.

Strategy

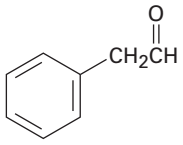
All IR spectra have many absorptions, but those useful for identifying specific functional groups are usually found in the region from 1500 cm^{-1} to 3300 cm^{-1}. Pay particular attention to the carbonyl region (1670 to

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

1780 cm^{-1}), the aromatic region (1660 to 2000 cm^{-1}), the triple-bond region (2000 to 2500 cm^{-1}), and the C–H region (2500 to 3500 cm^{-1}).

Solution

The spectrum shows an intense absorption at 1725 cm^{-1} due to a carbonyl group (perhaps an aldehyde, –CHO), a series of weak absorptions from 1800 to 2000 cm^{-1} characteristic of aromatic compounds, and a C–H absorption near 3030 cm^{-1}, also characteristic of aromatic compounds. In fact, the compound is phenylacetaldehyde.



Phenylacetaldehyde

PROBLEM 12-9

The IR spectrum of phenylacetylene is shown in **FIGURE 12-28**. What absorption bands can you identify?

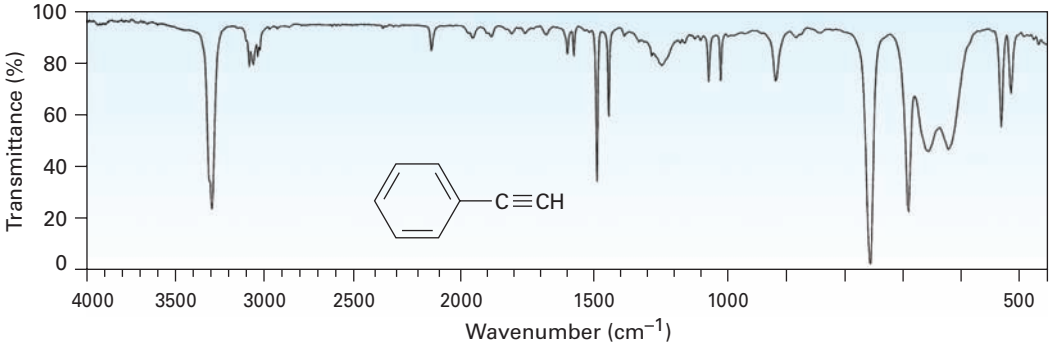
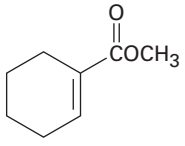


FIGURE 12-28 The IR spectrum of phenylacetylene, Problem 12-9.

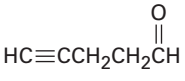
PROBLEM 12-10

Where might the following compounds have IR absorptions?

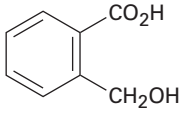
(a)



(b)

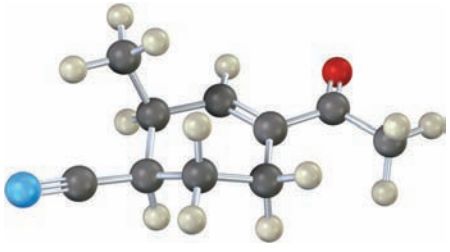


(c)



PROBLEM 12-11

Where might the following compound have IR absorptions?



Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

SOMETHING EXTRA

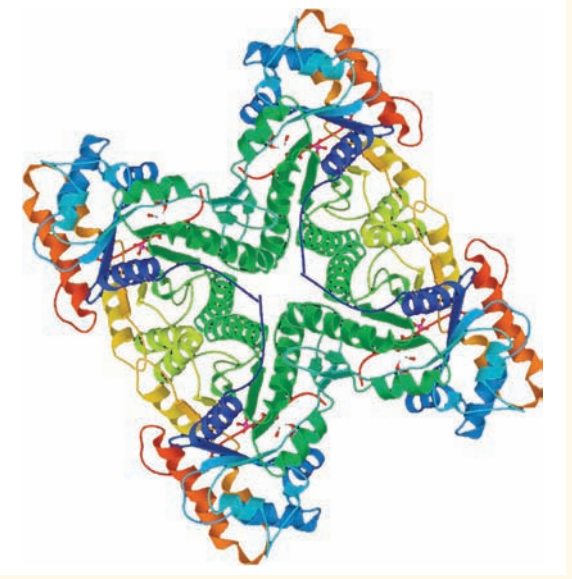
X-Ray Crystallography

The various spectroscopic techniques described in this and the next two chapters are enormously important in chemistry and have been fine-tuned to such a degree that the structure of almost any molecule can be found. Nevertheless, wouldn't it be nice if you could simply look at a molecule and "see" its structure with your eyes?

Determining the three-dimensional shape of an object around you is easy—you just look at it, let your eyes focus the light rays reflected from the object, and let your brain assemble the data into a recognizable image. If the object is small, you use a microscope and let the microscope lens focus the visible light. Unfortunately, there is a limit to what you can see, even with the best optical microscope. Called the diffraction limit, you can't see anything smaller than the wavelength of light you are using for the observation. Visible light has wavelengths of several hundred nanometers, but atoms in molecules have dimensions on the order of 0.1 nm. Thus, to "see" a molecule—whether a small one in the laboratory or a large, complex enzyme with a molecular weight in the tens of thousands—you need wavelengths in the 0.1 nm range, which corresponds to X rays.

Let's say that we want to determine the structure and shape of an enzyme or other biological molecule. The technique used is called *X-ray crystallography*. First, the molecule is crystallized (which often turns out to be the most difficult and time-consuming part of the entire process) and a small crystal of 0.4 to 0.5 mm on its longest axis is glued to the end of a glass fiber. The fiber and attached crystal are then mounted in an instrument called an X-ray diffractometer, which consists of a radiation source, a sample positioning and orienting device that can rotate the crystal in any direction, a detector, and a controlling computer.

Once mounted in the diffractometer, the crystal is irradiated with X rays, usually so-called CuK_α radiation with a wavelength of 0.154 nm. When the X rays strike the enzyme crystal, they interact with electrons in the molecule and are scattered into a diffraction pattern which, when detected and visualized, appears as a series of intense spots against a null background.



PDB ID: 1ALD, Gamblin, S.J. Davies, G.J. Grimes, J.M. Jackson, R.M. Littlechild, J.A. Watson, H.C. (1991) J. Mol. Biol. 219: 573-576.

The structure of human muscle fructose-1,6-bisphosphate aldolase, as determined by X-ray crystallography and downloaded from the Protein Data Bank, 1ALD.

Manipulation of the diffraction pattern to extract three-dimensional molecular data is a complex process, but the final result is an electron-density map of the molecule. Because electrons are largely localized around atoms, any two centers of electron density located within bonding distance of each other are assumed to represent bonded atoms, leading to a recognizable chemical structure. So important is this structural information for biochemistry that an online database of more than 100,000 biological substances has been created. Operated by Rutgers University and funded by the U.S. National Science Foundation, the Protein Data Bank (PDB) is a worldwide repository for processing and distributing three-dimensional structural data for biological macromolecules. We'll see how to access the PDB in the Chapter 26 *Something Extra*.

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

SUMMARY

Finding the structure of a new molecule, whether a small one synthesized in the laboratory or a large protein found in living organisms, is central to the progression of chemistry and biochemistry. The structure of an organic molecule is usually determined using spectroscopic methods, including mass spectrometry and infrared spectroscopy. **Mass spectrometry (MS)** tells the molecular weight and formula of a molecule; **infrared (IR) spectroscopy** identifies the functional groups present in the molecule.

In small-molecule mass spectrometry, molecules are first ionized by collision with a high-energy electron beam. The ions then fragment into smaller pieces, which are magnetically sorted according to their mass-to-charge ratio (m/z). The ionized sample molecule is called the *molecular ion*, M^+, and measurement of its mass gives the molecular weight of the sample. Structural clues about unknown samples can be obtained by interpreting the fragmentation pattern of the molecular ion. Mass-spectral fragmentations are usually complex, however, and interpretation is often difficult. In biological mass spectrometry, molecules are protonated using either electrospray ionization (ESI) or matrix-assisted laser desorption ionization (MALDI), and the protonated molecules are separated by time-of-flight (TOF) mass analysis.

Infrared spectroscopy involves the interaction of a molecule with **electromagnetic radiation**. When an organic molecule is irradiated with infrared energy, certain **frequencies** are absorbed by the molecule. The frequencies absorbed correspond to the amounts of energy needed to increase the amplitude of specific molecular vibrations such as bond stretching and bending. Since every functional group has a characteristic combination of bonds, every functional group has a characteristic set of infrared absorptions. For example, the terminal alkyne ≡C–H bond absorbs IR radiation of 3300 cm^{-1}, and the alkene C=C bond absorbs in the range 1640 to 1680 cm^{-1}. By observing which frequencies of infrared radiation are absorbed by a molecule and which are not, it's possible to determine the functional groups a molecule contains.

KEY WORDS

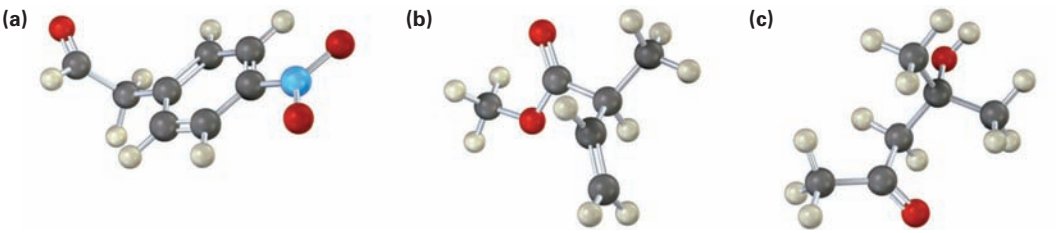
absorption spectrum, 370
amplitude, 369
base peak, 356
electromagnetic spectrum, 368
frequency, ν, 369
hertz, Hz, 369
infrared (IR) spectroscopy, 371
mass spectrometry (MS), 355
parent peak, 357
quadrupole mass analyzer, 356
wavelength, λ, 369
wavenumber $\tilde{\nu}$, 371

EXERCISES

VISUALIZING CHEMISTRY

(Problems 12-1–12-11 appear within the chapter.)

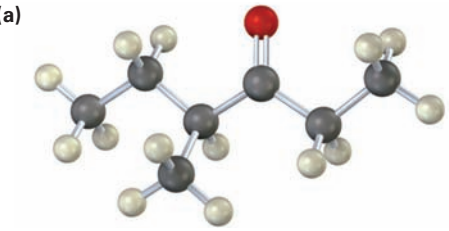
12-12 Where in the IR spectrum would you expect each of the following molecules to absorb?



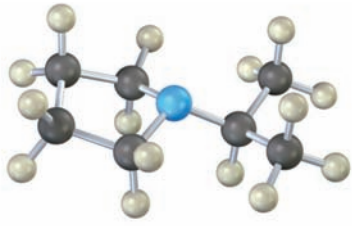
Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

12-13 Show the structures of the fragments you would expect in the mass spectra of the following molecules:

(a)



(b)



ADDITIONAL PROBLEMS

Mass Spectrometry

12-14 Propose structures for compounds that fit the following mass-spectral data:

(a) A hydrocarbon with $M^+ = 132$ **(b)** A hydrocarbon with $M^+ = 166$

(c) A hydrocarbon with $M^+ = 84$

12-15 Write molecular formulas for compounds that show the following molecular ions in their high-resolution mass spectra, assuming that C, H, N, and O might be present. The exact atomic masses are: 1.007 83 (^{1}H), 12.000 00 (^{12}C), 14.003 07 (^{14}N), 15.994 91 (^{16}O).

(a) $M^+ = 98.0844$ **(b)** $M^+ = 123.0320$

12-16 Camphor, a saturated monoketone from the Asian camphor tree, is used among other things as a moth repellent and as a constituent of embalming fluid. If camphor has $M^+ = 152.1201$ by high-resolution mass spectrometry, what is its molecular formula? How many rings does camphor have?

12-17 The *nitrogen rule* of mass spectrometry says that a compound containing an odd number of nitrogens has an odd-numbered molecular ion. Conversely, a compound containing an even number of nitrogens has an even-numbered M^+ peak. Explain.

12-18 In light of the nitrogen rule mentioned in Problem 12-17, what is the molecular formula of pyridine, $M^+ = 79$?

12-19 Nicotine is a diamino compound isolated from dried tobacco leaves. Nicotine has two rings and $M^+ = 162.1157$ by high-resolution mass spectrometry. Give a molecular formula for nicotine, and calculate the number of double bonds.

12-20 The hormone cortisone contains C, H, and O, and shows a molecular ion at $M^+ = 360.1937$ by high-resolution mass spectrometry. What is the molecular formula of cortisone? (The degree of unsaturation for cortisone is 8.)

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

12-21 Halogenated compounds are particularly easy to identify by their mass spectra because both chlorine and bromine occur naturally as mixtures of two abundant isotopes. Recall that chlorine occurs as ^{35}Cl (75.8%) and ^{37}Cl (24.2%); and bromine occurs as ^{79}Br (50.7%) and ^{81}Br (49.3%). At what masses do the molecular ions occur for the following formulas? What are the relative percentages of each molecular ion?

(a) Bromomethane, CH_3Br **(b)** 1-Chlorohexane, $C_6H_{13}Cl$

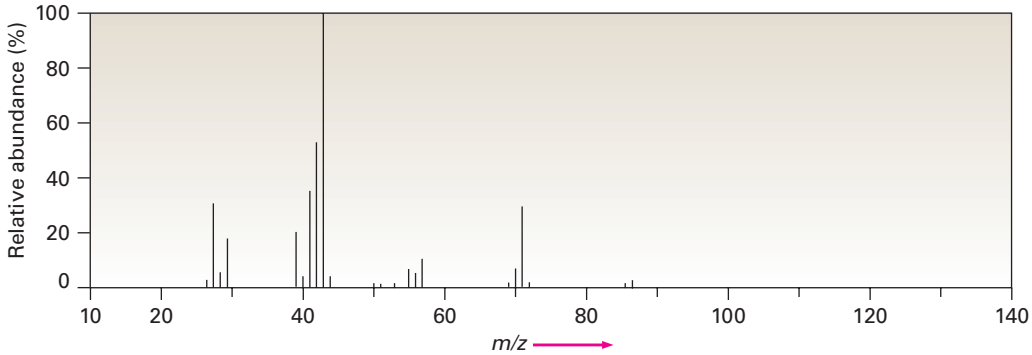
12-22 By knowing the natural abundances of minor isotopes, it's possible to calculate the relative heights of M^+ and M + 1 peaks. If ^{13}C has a natural abundance of 1.10%, what are the relative heights of the M^+ and M + 1 peaks in the mass spectrum of benzene, C_6H_6?

12-23 Propose structures for compounds that fit the following data:

(a) A ketone with $M^+ = 86$ and fragments at $m/z = 71$ and $m/z = 43$

(b) An alcohol with $M^+ = 88$ and fragments at $m/z = 73$, $m/z = 70$, and $m/z = 59$

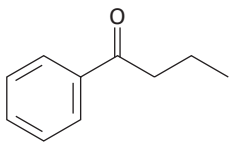
12-24 2-Methylpentane (C_6H_{14}) has the mass spectrum shown. Which peak represents M^+? Which is the base peak? Propose structures for fragment ions of $m/z = 71$, 57, 43, and 29. Why does the base peak have the mass it does?



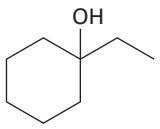
12-25 Assume that you are in a laboratory carrying out the catalytic hydrogenation of cyclohexene to cyclohexane. How could you use a mass spectrometer to determine when the reaction is finished?

12-26 What fragments might you expect in the mass spectra of the following compounds?

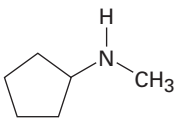
(a)



(b)



(c)



Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Infrared Spectroscopy

12-27 How might you use IR spectroscopy to distinguish among the three isomers 1-butyne, 1,3-butadiene, and 2-butyne?

12-28 Would you expect two enantiomers such as (*R*)-2-bromobutane and (*S*)-2-bromobutane to have identical or different IR spectra? Explain.

12-29 Would you expect two diastereomers such as *meso*-2,3-dibromobutane and (2*R*,3*R*)-dibromobutane to have identical or different IR spectra? Explain.

12-30 Propose structures for compounds that meet the following descriptions:

(a) C_5H_8, with IR absorptions at 3300 and 2150 cm^{-1}

(b) C_4H_8O, with a strong IR absorption at 3400 cm^{-1}

(c) C_4H_8O, with a strong IR absorption at 1715 cm^{-1}

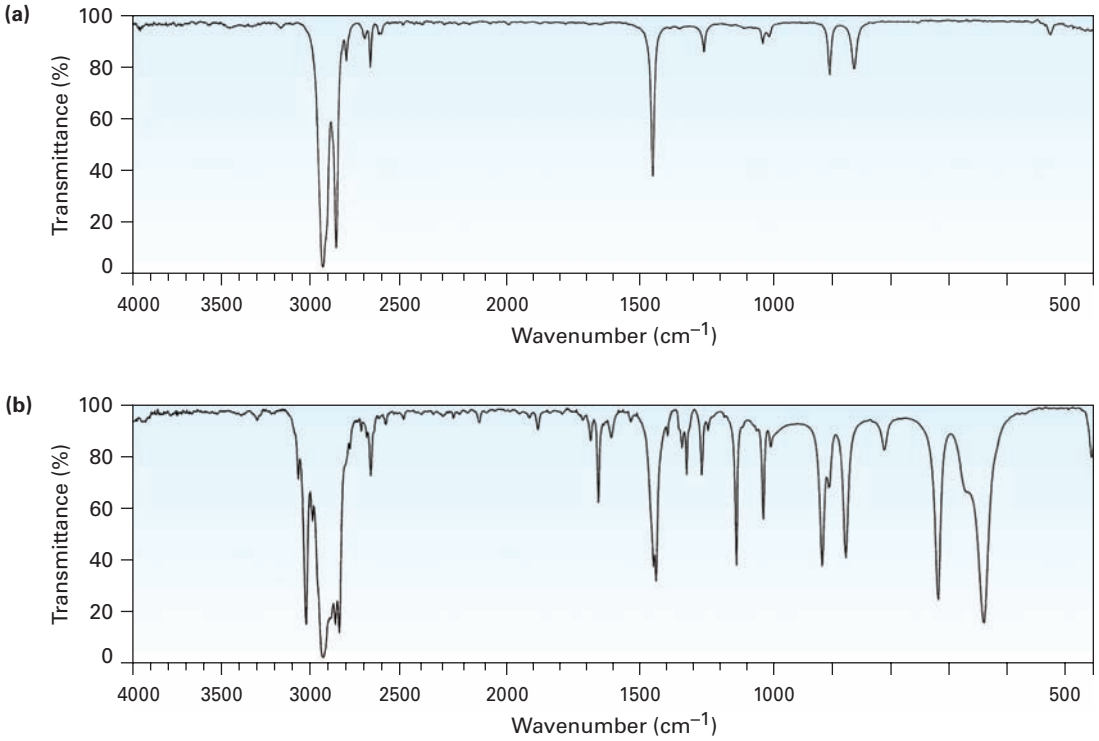
(d) C_8H_{10}, with IR absorptions at 1600 and 1500 cm^{-1}

12-31 How could you use infrared spectroscopy to distinguish between the following pairs of isomers?

(a) $HC{\equiv}CCH_2NH_2$ and $CH_3CH_2C{\equiv}N$

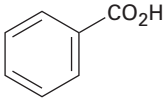
(b) CH_3COCH_3 and CH_3CH_2CHO

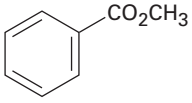
12-32 Two infrared spectra are shown. One is the spectrum of cyclohexane, and the other is the spectrum of cyclohexene. Identify them, and explain your answer.

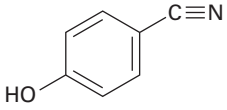


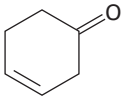
Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

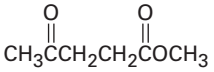
12-33 At what approximate positions might the following compounds show IR absorptions?

(a) 

(b) 

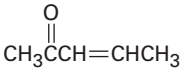
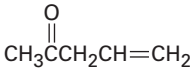
(c) 

(d) 

(e) 

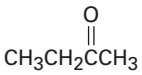
12-34 How would you use infrared spectroscopy to distinguish between the following pairs of constitutional isomers?

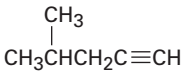
(a) $CH_3C{\equiv}CCH_3$ and $CH_3CH_2C{\equiv}CH$

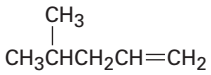
(b)  and 

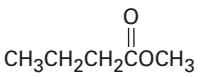
(c) $H_2C{=}CHOCH_3$ and CH_3CH_2CHO

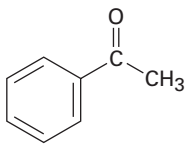
12-35 At what approximate positions might the following compounds show IR absorptions?

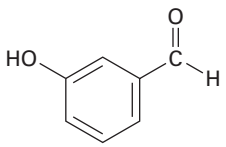
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

12-36 Assume that you are carrying out the dehydration of 1-methylcyclohexanol to yield 1-methylcyclohexene. How could you use infrared spectroscopy to determine when the reaction is complete?

12-37 Assume that you are carrying out the base-induced dehydrobromination of 3-bromo-3-methylpentane (Section 11-7) to yield an alkene. How could you use IR spectroscopy to tell which of three possible elimination products is formed, if one includes *E*/*Z* isomers?

General Problems

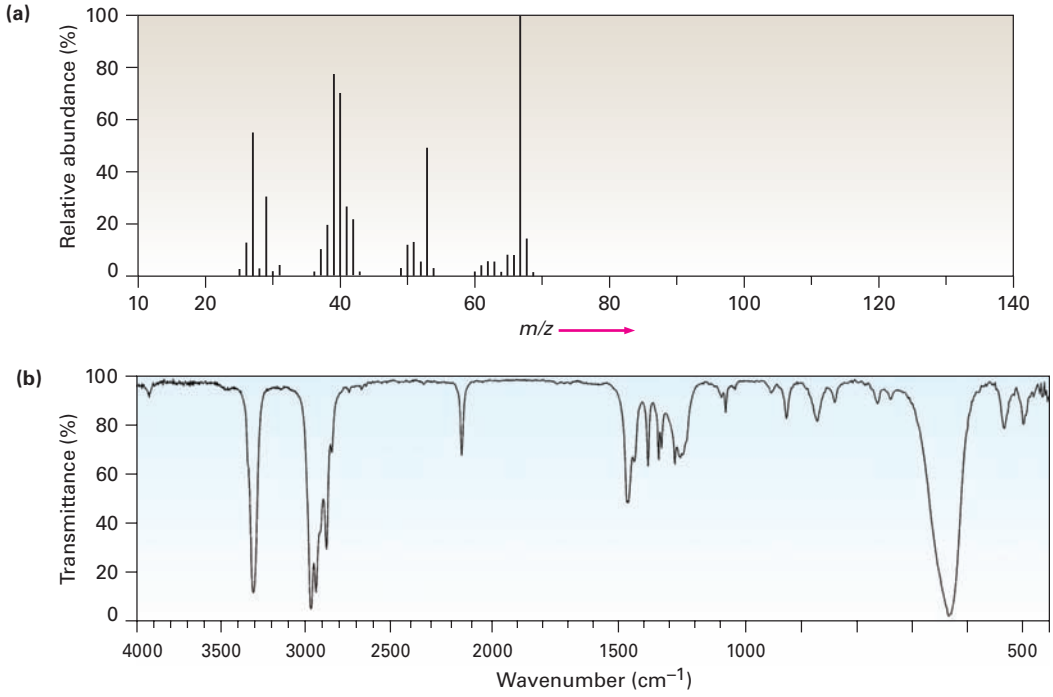
12-38 Which is stronger, the C=O bond in an ester (1735 cm^{-1}) or the C=O bond in a saturated ketone (1715 cm^{-1})? Explain.

12-39 Carvone is an unsaturated ketone responsible for the odor of spearmint. If carvone has $M^+ = 150$ in its mass spectrum and contains three double bonds and one ring, what is its molecular formula?

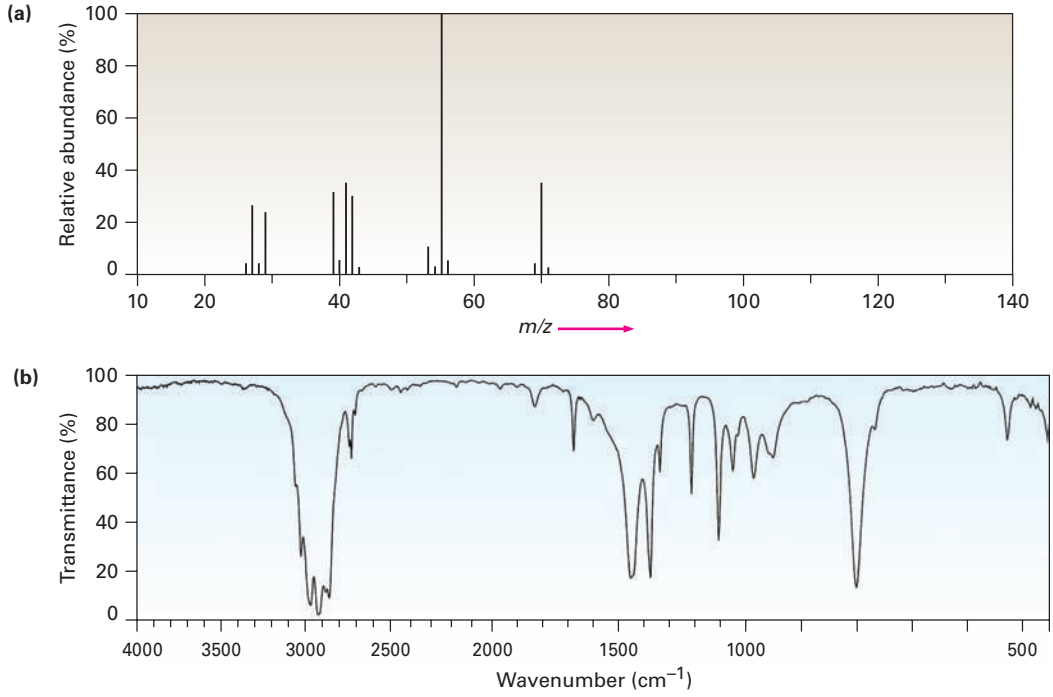
12-40 Carvone (Problem 12-39) has an intense infrared absorption at 1690 cm^{-1}. What kind of ketone does carvone contain?

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

12-41 The mass spectrum **(a)** and the infrared spectrum **(b)** of an unknown hydrocarbon are shown. Propose as many structures as you can.



12-42 The mass spectrum **(a)** and the infrared spectrum **(b)** of another unknown hydrocarbon are shown. Propose as many structures as you can.



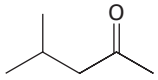
Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

12-43 Propose structures for compounds that meet the following descriptions:

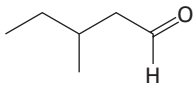
(a) An optically active compound $C_5H_{10}O$ with an IR absorption at 1730 cm^{-1}

(b) A non-optically active compound C_5H_9N with an IR absorption at 2215 cm^{-1}

12-44 4-Methyl-2-pentanone and 3-methylpentanal are isomers. Explain how you could tell them apart, both by mass spectrometry and by infrared spectroscopy.

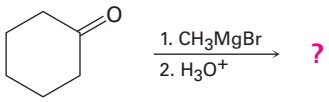


4-Methyl-2-pentanone



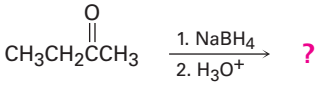
3-Methylpentanal

12-45 Grignard reagents undergo a general and very useful reaction with ketones. Methylmagnesium bromide, for example, reacts with cyclohexanone to yield a product with the formula $C_7H_{14}O$. What is the structure of this product if it has an IR absorption at 3400 cm^{-1}?



Cyclohexanone

12-46 Ketones undergo a reduction when treated with sodium borohydride, $NaBH_4$. What is the structure of the compound produced by reaction of 2-butanone with $NaBH_4$ if it has an IR absorption at 3400 cm^{-1} and $M^+ = 74$ in the mass spectrum?

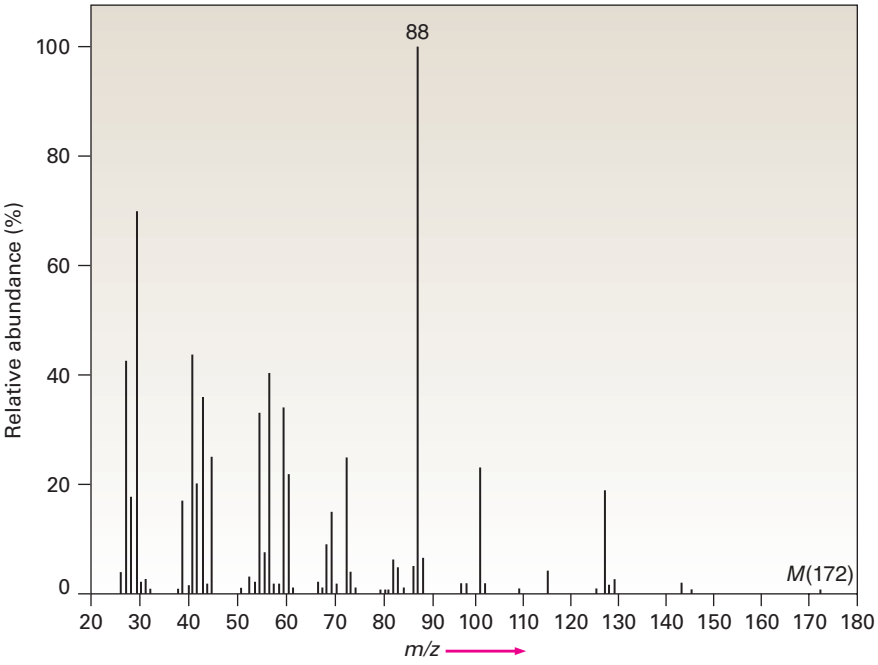


2-Butanone

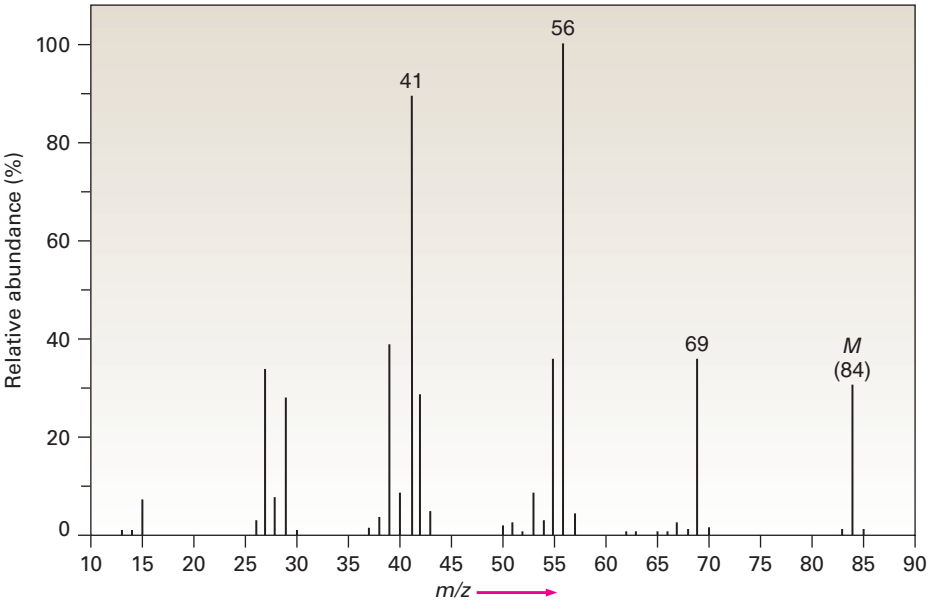
12-47 Nitriles, R–C≡N, undergo a hydrolysis reaction when heated with aqueous acid. What is the structure of the compound produced by hydrolysis of propanenitrile, $CH_3CH_2C{\equiv}N$, if it has IR absorptions from 2500–3100 cm^{-1} and at 1710 cm^{-1}, and has $M^+ = 74$?

Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

12-48 The infrared spectrum of the compound with the mass spectrum shown below lacks any significant absorption above 3000 cm^{-1}. There is a prominent peak near 1740 cm^{-1} and another strong peak near 1200 cm^{-1}. Propose a structure consistent with the data.

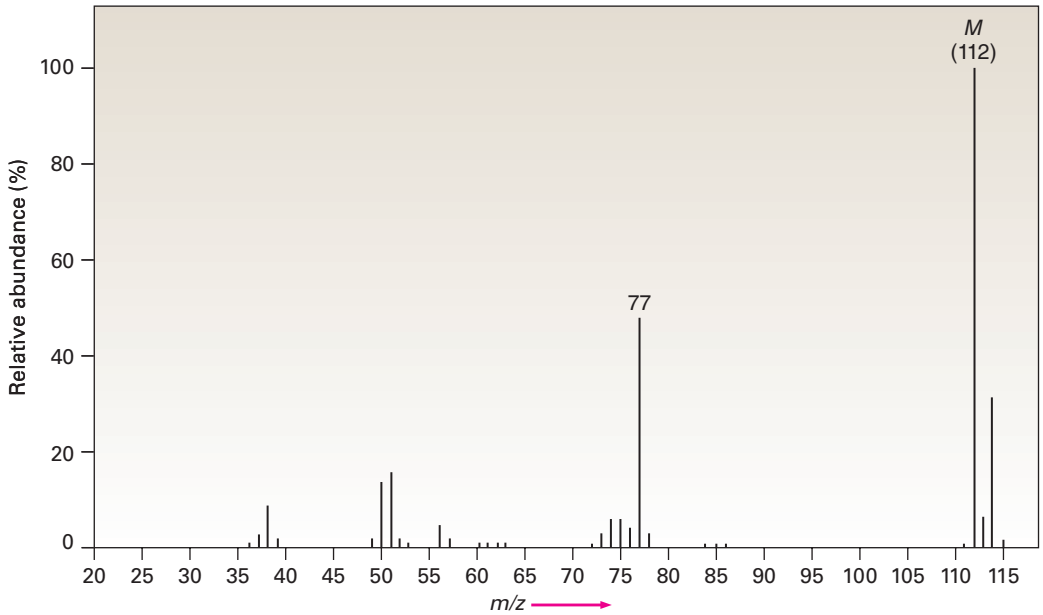


12-49 The infrared spectrum of the compound with the mass spectrum shown below has a medium-intensity peak at about 1650 cm^{-1}. There is also a C–H out-of-plane bending peak near 880 cm^{-1}. Propose a structure consistent with the data.



Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

12-50 The infrared spectrum of the compound with the mass spectrum shown below has strong absorbances at 1584, 1478, and 1446 cm^{-1}. Propose a structure consistent with the data.



Copyright 2016 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.